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Bimanes and Related Heterocycles as Laser Dyes

FINAL REPORT

J. H. Boyer

January 10, 1991

U. S. Army Research Office

Contract or Grant Number: DAAL03-89-K-0161

University of New Orleans

Reprint (50 copies):

Chun M. Lau, Ieva Politzer, Kannappan Thangaraj, Govindarajulu Kumar, Vayalakkavoor T. Ramakrishnan, Edwin D. Stevens, Joseph H.Boyer and Theodore G. Pavlopoulos, "Bimanes (1,5–Diazabicyclo[3.3.0]octadienediones): Laser Activity in *syn*–Bimanes", Heteroatom Chemistry, 1990, 1, 195.

Reprint (50 copies):

Mayur Shah, Kannappan Thangaraj, Mou-Ling Soong, Lionel T. Wolford, Joseph H. Boyer, Ieva R. Politzer, and Theodore G. Pavlopoulos, "Pyrromethene–BF_2 Complexes as Laser Dyes: 1.", Heteroatom Chemistry, 1990, 1, 389.

Statement of the Problem: (see Reprints)

Summary: (see Reprints)

Publications and Technical Reports: (see Reprints)

Inventions: None

Bibliography: (see Reprints)

Appendixes: None

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	Jan. 10, 1991	

4. TITLE AND SUBTITLE
Bimanes and Related Heterocycles as Laser Dyes

5. FUNDING NUMBERS
DAAL03-89-K-0161

6. AUTHOR(S)
J. H. Boyer

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of New Orleans
New Orleans, LA 70148

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
ARO 27529.1-CH

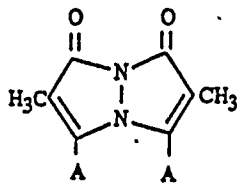
11. SUPPLEMENTARY NOTES
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

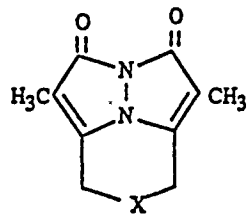
12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

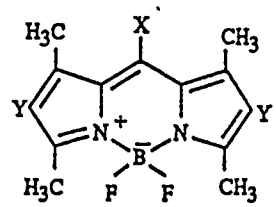
The relative efficiencies (RE) for laser activity in the spectral region 500-530 nm were obtained for 37 *syn*-bimanes by reference to coumarin 30 (RE 100). RE > 80 was observed for bimanes 1 - 4.



1 A = $CH_2O_2CCH_3$
2 A = $CH_2(O)P(OCH_3)_2$



3 X = $C(CO_2CH_3)_2$
4 X = $C(CO_2C_2H_5)_2$



5 X = CH_3, Y = SO_3Na
6 X = CH_3, Y = C_2H_5

The relative efficiencies (RE) for laser activity in the spectral region 520-620 nm were obtained for over 20 pyrromethene-BF_2 complexes (P-BF_2) by reference to rhodamine 6G (RE 100). The complexes 5 and 6 were the first dyes to surpass rhodamine 6G and are now the most power efficient laser dyes known. Bimanes 1 and 3 and P-BF_2 5 and 6 are now commercially available (DEKK-TEC, Inc., New Orleans, LA).

14. SUBJECT TERMS	15. NUMBER OF PAGES
Unknown	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

91 2 15 159

Heteroatom Chemistry
Volume 1, Number 3, 1990

Bimanes (1,5-Diazabicyclo[3.3.0]octadienediones): Laser Activity in *syn*-Bimanes

Chun M. Lau, Kannappan Thangaraj, Govindarajulu Kumar, Vayalakkavoor T. Ramakrishnan, Edwin D. Stevens, and Joseph H. Boyer*
Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148, U.S.A.
Ieva R. Politzer
Department of Chemistry, Xavier University, New Orleans, Louisiana 70125, U.S.A.
Theodore G. Pavlopoulos
U.S. Naval Ocean Systems Center, San Diego, California 92152, U.S.A.

Received 6 October 1989.

ABSTRACT

The conversion of 3-methyl-4-benzyl-4-chloro-2-pyrazolin-5-one ***10b*** *was catalyzed by a mixture of potassium fluoride and alumina to give* syn-(*methyl,benzyl*)*bimane* ***6*** *(62%) without detectable formation of the* anti *isomer* ***A6*** *[a 1 : 1 mixture (87%) of the isomers* ***6*** *and* ***A6*** *was obtained when the catalyst was potassium carbonate]. In a similar reaction* syn-(*methyl,carboethoxymethyl*)*bimane* ***7*** *(15%) with the* anti *isomer* ***A7*** *(36%) was obtained from 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one* ***10c.*** syn-(*Methyl,β-acetoxyethyl*)*bimane* ***8*** *(70%) was obtained from 3-methyl-4-β-acetoxyethyl-4-chloro-2-pyrazolin-5-one* ***10d*** *(potassium carbonate catalysis) and was converted by hydrolysis to* syn-(*methyl,β-hydroxyethyl*)*bimane* ***9*** *(40%). Acetyl nitrate (nitric acid in acetic anhydride) converted* anti-(*amino,hydrogen*)*bimane* ***11*** *to* anti-(*amino,nitro*)*bimane* ***15*** *(91%),* anti-(*methyl,hydrogen*)*bimane* ***13*** *to* anti-(*methyl,nitro*)(*methyl,hydrogen*)*bimane* ***16*** *(57%), and degraded* syn-(*methyl,hydrogen*)*bimane* ***12*** *to an intractable mixture. Treatment with trimethyl phosphite converted* syn-(*bromomethyl,methyl*)*bimane* ***17*** *to* syn-(*dimethoxyphosphinylmethyl,methyl*)*bimane* ***18*** *(78%) that was further converted to* syn-(*styryl,methyl*)*bimane* ***19*** *(29%) in a condensation reaction with benzaldehyde. Treatment with acryloyl chloride converted* syn-(*hydroxymethyl,methyl*)*bimane* ***20*** *to its acrylate ester* ***21*** *(22%). Stoichiometric bromination of* syn-(*methyl,methyl*)*bimane* ***1*** *gave a monobromo derivative that was converted* in situ *by treatment with potassium acetate to* syn-(*acetoxymethyl,methyl*)(*methyl,methyl*)*bimane* ***47.*** *N-Amino-μ-amino-*syn-(*methylene,methyl*)*bimane* ***24*** *(68%) was obtained from a reaction between the dibromide* ***17*** *and hydrazine. Derivatives of the hydrazine* ***24*** *included a perchlorate salt and a hydrazone* ***25*** *derived from acetone. Dehydrogenation of* syn-(*tetramethylene*)*bimane* ***26*** *by treatment with dichlorodicyanobenzoquinone (DDQ) gave* syn-(*benzo,tetramethylene*)*bimane* ***27*** *(58%) and* syn-(*benzo*)*bimane* ***28*** *(29%). Bromination of the bimane* ***26*** *gave a dibromide* ***29*** *(92%) that was also converted by treatment with DDQ to* syn-(*benzo*)*bimane* ***28.*** *Treatment with palladium (10%) on charcoal dehydrogenated 5,6,10,11-tetrahydro-7*H,9H-*benz[6,7]indazol[1,2-a]benz[g]indazol-7,9-dione* ***35*** *to* syn-(*α-naphtho*)*bimane* ***36*** *(71%). The bimane* ***35*** *was prepared from 1,2,3,4-tetrahydro-1-oxo-2-naphthoate* ***37*** *by stepwise*

* To whom correspondence should be addressed.

1042-7163/90/$3.50 + .25

treatment with hydrazine to give 1,2,4,5-tetrahydro-3H-benz[g]indazol-3-one ***38****, followed by chlorine to give 3a-chloro-2,3a,4,5-tetrahydro-3H-benz[g]indazol-3-one* ***39****, and base. Dehydrogenation over palladium converted the indazolone* ***34*** *to 1H-benz[g]indazol-3-ol* ***36****. Helicity for the hexacyclic* syn-(α-*naphtho)bimane* ***36*** *was confirmed by an analysis based on molecular modeling.*

The relative efficiencies (RE) for laser activity in the spectral region 500–530 nm were obtained for 37 syn-*bimanes by reference to coumarin 30 (RE 100): RE > 80 for* syn-*bimanes* ***3, 5, 18,*** *and* μ-(*dicarbomethoxy)methylene*-syn-(*methylene,methyl)bimane* ***22:*** *RE 20–80: for* syn-*bimanes* ***1, 2, 4, 20, 24, 26,*** *and* μ-*thia*-syn-(*methylene,methyl)bimane* ***50:*** *and RE 0-20 for 26* syn-*bimanes. The bimane dyes tended to be more photostable and more water-soluble than coumarin 30. The diphosphonate* ***18*** *in dioxane showed laser activity at 438 nm and in water at 514 nm. Presumably helicity, that was demonstrated by molecular modeling, brought about a low fluorescence intensity for* syn-(α-*naphtho)bimane* ***36,*** *Φ0.1, considerably lower than obtained for* syn-(*benzo)bimane* ***28,*** *Φ0.9.*

INTRODUCTION

Following its discovery in 1966 the dye laser [1] depended on the availability of laser dyes to provide coherent light over the spectral region from ultraviolet (UV) to infrared (IR). This laser activity was obtained from cyanine, xanthene (including rhodamine and fluoroscein), triarylmethane, acridine, azine, and chlorophyll dyes; linear and condensed polybenzenoid molecules; and certain heterocycles that included coumarins, quinolones, oxazoles, pyrazolines, and furans. In 1984, over 600 laser dyes were listed [2].

Parameters for a laser dye included high quantum fluorescence yield, (generally $\Phi > 0.7$), minimal overlap of fluorescence with onset of absorption (S-S) and triplet-triplet (T-T) spectral regions, photostability, efficiency in power output, favorable solubility and interaction with the solvent, and availability [3]. Other factors also contributed to the laser performance. Aqueous solutions of a dye (10^{-4} molar was generally desirable) offered the superior thermo-optic properties of water that often improved laser activity [5c]. Groups that enhanced intersystem crossing ($S_1 \rightarrow T_1$) through the heavy atom effect could interfere with laser activity and were generally avoided [3]. It was sometimes assumed that somewhat less than expected laser power output was the result of (1) nonradiative transfer ($S_1 \rightarrow S_0$), (2) loss of electronic excitation through reversible charge transfer with the chromophore, and/or (3) self-quenching through dye aggregation [3]. About 125 tunable laser dyes more or less satisfied these special conditions and became commercially available to cover the region from 300–1200 nm [4].

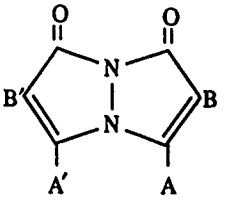
Other investigations led us to examine *syn*-bimanes (1,5-diazabicyclo[3.3.0]octadiene-2,8-diones) as laser dyes. Kosower introduced a system of trivial nomenclature for the bimanes based on substitution types. Type I: *syn*-(A,B)bimanes, Type II: *syn*-(A,B)(A′,B′)bimanes, Type III: μ-X-*syn*-(methylene,methyl)bimanes, Type IV: *anti*-(A,B)bimanes, and Type V: *anti*-(A,B)(A′,B′)bimanes were adopted for this report [6, 7].

Laser activity in the spectral region 500–530 nm from *syn*-(methyl,methyl)bimane **1** was reported in 1986 [5a]. The discovery of similar activity from *syn*-(methyl,chloro)bimane **2**, *syn*-(acetoxymethyl,methyl)bimane **3**, *syn*-(fluoromethyl,methyl)bimane **4**, and μ-(dicarboethoxy) methylene-*syn*-(methylene,methyl)bimane **5** followed rapidly [5b–d]. In our ongoing search for laser dyes it became desirable to examine greater diversification in substitution patterns in *syn*-bimanes.

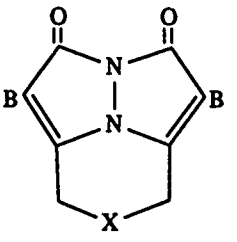
syn-*BIMANE DYE PREPARATIONS AND PROPERTIES*

Background Information

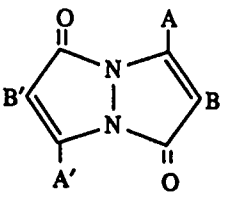
Variation in substitution patterns in *syn*-bimanes has remained limited. In the Kosower scheme for their synthesis chlorination of a pyrazolinone followed by treatment with a base (potassium carbonate or a tertiary amine) brought about the forma-



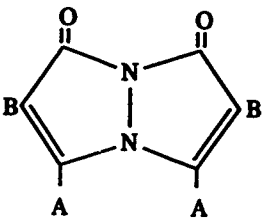
Type I: A,B = A′,B′
Type II: A,B ≠ A′,B′



Type III: X = C,N,S



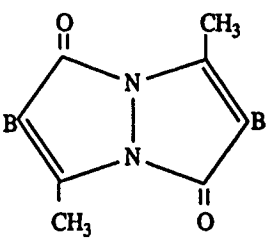
Type IV: A,B = A′,B′
Type V: A,B ≠ A′,B′



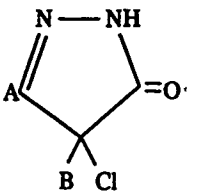
Compound	A	B	Cpd	A	B
1	CH_3	CH_3	**12**	CH_3	H
2	CH_3	Cl	**17**	$BrCH_2$	CH_3
3	$CH_3CO_2CH_2$	CH_3	**18**	$(CH_3O)_2P(O)CH_2$	CH_3
4	FCH_2	CH_3	**19**	$C_6H_5CH{=}CH$	CH_3
6	CH_3	$CH_2C_6H_5$	**20**	$HOCH_2$	CH_3
7	CH_3	$CH_2CO_2C_2H_5$	**21**	$CH_2{=}CHOCOCH_2$	CH_3
8	CH_3	$CH_2CH_2O_2CCH_3$	**43**	CH_3	C_6H_5
9	CH_3	CH_2CH_2OH	**44**	C_6H_5	Cl
			45	C_2H_5OCO	Cl

tion of mixtures of *syn*- and *anti*-bimanes, eq. (1) [6–8]. Selected conversions afforded preparative amounts of *syn*-bimanes with a limited range of substituents. *syn*-Bimanes with strong electron donating or withdrawing substituents were not prepared by this method and remain largely unknown. The chemical reactivity needed for further conversion of a substituent, e.g., methyl to acetoxymethyl [8] was restricted to the short axis where substituents ran parallel with the NN bond.

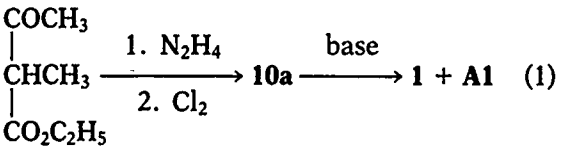
Chemical reactivity, "normal" positions of nuclear magnetic resonance (NMR) signals, and the occurrence of planar and nonplanar molecules in the crystal were properties that supported the perception of *syn*- and *anti*-bimanes as examples of α,β-unsaturated amide systems with no implication of "aromatic character" [6]. The fluorescence, $\Phi > 0.7$, from many *syn*-bimanes was, nevertheless, assumed to be a property of aromaticity insofar as strong fluorescence from an organic compound that was not aromatic has remained virtually unknown [5b]. A weak fluorescence from *anti*-bimanes [6] was shared with other pyrazolinones [9], γ-pyridones [10], maleimides [11], and presumably other quasiaromatic cyclic amides and hydrazides. A strong phosphorescence was noted for *anti*- but not for *syn*-bimanes [6].



A1 B = CH_3
A6 B = $CH_2C_6H_5$
A7 B = $CH_2CO_2C_2H_5$



Compound	A	B
10a	CH_3	CH_3
10b	CH_3	$CH_2C_6H_5$
10c	CH_3	$CH_2CO_2C_2H_5$
10d	CH_3	$CH_2CH_2O_2CCH_3$
10e	H	$CO_2C_2H_5$



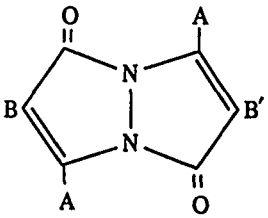
$$\begin{array}{l}\text{COCH}_3\\ |\\ \text{CHCH}_3\\ |\\ \text{CO}_2\text{C}_2\text{H}_5\end{array} \xrightarrow[2.\ \text{Cl}_2]{1.\ \text{N}_2\text{H}_4} \mathbf{10a} \xrightarrow{\text{base}} \mathbf{1} + \mathbf{A1} \quad (1)$$

Long Axis (Perpendicular to the NN Bond) Substitution

syn-(Methyl,benzyl)bimane **6** was prepared from 3-methyl-4-benzyl-4-chloro-2-pyrazolin-5-one **10b** (obtained from ethyl benzylacetoacetate by treatment with hydrazine followed by chlorination) under the influence of a novel catalyst [12] that was provided by a mixture of potassium fluoride and alumina. Formation of the *anti*-isomer **A6** was not detected; however, a mixture (1 : 1) of the isomers **6** and **A6** was obtained when potassium carbonate was the catalyst. In related conversions 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one **10c** (from diethyl acetosuccinate) gave *syn*-(methyl,carboethoxymethyl)bimane **7** along with the *anti* isomer **A7**, and 3-methyl-4-β-acetoxyethyl-4-chloro-2-pyrazolin-5-one **10d** (from ethyl β-acetoxyethylacetoacetate) gave *syn*-(methyl,β-acetoxyethyl)bimane **8**. Hydrolysis converted the latter to

syn-(methyl,β-hydroxyethyl)bimane **9.** Attempts to obtain *syn*-(hydrogen,carboethyoxy)bimane from ethoxymethylenemalonic ester were unsuccessful. Treatment with hydrazine converted the ester to a pyrazolinone that underwent chlorination to a product thought to be the chloropyrazolinone **10e**; however, the latter in the presence of base resisted conversion to a bimane.

To enhance bimane functionality an exploratory investigation of the aromatic nitration of *anti*-(amino,hydrogen)bimane **11** (the *syn* isomer is unknown) and *syn*- and *anti*-(methyl,hydrogen)bimanes **12** and **13** was undertaken. The *anti*-bimane **11** was obtained from N,N'-dicyanoacetohydrazide **14** [$(NHCOCH_2CN)_2$] by cyclization in the presence of sodium bicarbonate [13]. Acetyl nitrate (explosive above 50°C), prepared in situ from a mixture of nitric acid (90%) and acetic anhydride, converted the *anti*-bimane **11** to *anti*-(amino,nitro)bimane **15**, a structure assignment supported by IR, ^{13}C NMR, EI-MS, and elemental analysis. Similar treatment converted *anti*-(methyl,hydrogen)bimane **13** [5] to *anti*-(methyl,nitro)(methyl,hydrogen)bimane **16**. *syn*-(Methyl,hydrogen)bimane **12** [5] was completely converted by similar treatment to an intractable mixture that contained no more than a trace amount of a solid thought to be a mononitro derivative on the basis of M^+ 209 in the EI-MS. These aromatic substitution reactions resembled nitrations of pyrazolinones, hydroxy-, and aminopyrazoles [14] and tended to support quasiaromaticity of the bimane ring systems (see above).



11 A = NH_2, B = B' = H
13 A = CH_3, B = B' = H
15 A = NH_2, B = B' = NO_2
16 A = CH_3, B = NO_2, B' = H

Attempts to oxidize amino groups in bimanes **11** and **15** to nitro groups were unsuccessful and led instead to intractable mixtures. An unidentified product isolated as a hydrated dipotassium salt $C_6N_4O_8K_2 \cdot 1.5\ H_2O$ from a treatment of diaminodinitrobimane **15** with potassium superoxide represented the oxidation level of a dihydroxydinitrobimane, in which hydroxyl groups had replaced amino groups. A hydrated sodium salt of a dihydroxydinitro-bimane $C_6H_4O_8Na_2 \cdot 1.5\ H_2O$, was previously obtained in an oxidation of the corresponding dioxime [15].

The accessibility of substituted *syn*-bimanes was restricted by degradation of the bimane structure when treated under mild conditions with either an oxidizing reagent or an acid and, as previously reported [6], by ring opening and conversion under alkaline conditions.

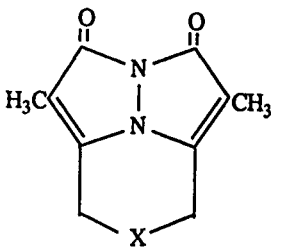
Short Axis (Parallel to the NN Bond) Substitution

Generally substituent variation proceeded from the nonfluorescent *syn*-(bromomethyl,methyl)bimane **17** [obtained from *syn*-(methyl,methyl)bimane **1** by bromination [7]. Conversion of the dibromide **17** to *syn*-(dimethoxyphosphinylmethyl,methyl)bimane **18** was brought about by treatment with trimethylphosphite. A need for polymerizable *syn*-bimane monomers to be formulated into glassy polymer slugs led to the preparation of *syn*-(styryl,methyl) bimane **19** (from the diphosphonate **18** and benzaldehyde) and the acrylate ester **21** of *syn*-(hydroxymethyl,methyl)bimane **20** (from the dibromide **17** by treatment with alkali followed by esterification of the glycol **20** with acryloyl chloride). Laser activity from dyes in polymeric glasses [16] will be described elsewhere.

Stoichiometry controlled a monobromination of the bimane **1** [6, 8]. Without isolation the bromide was treated with potassium acetate to give *syn*-(acetoxymethyl,methyl)(methyl,methyl) bimane **47.**

μ-Bridged syn-*Bimanes*

Ring closure between short axis methyl substituents by a one atom bridge afforded μ-bridged *syn*-bimanes [7]. These tricyclic heterocycles were generally obtained from the dibromide **17** in reactions with nucleophiles. We repeated Kosower's preparation of μ-(dicarboethoxy)methylene-*syn*-(methylene,methyl)bimane **5** from the dibromide **17** in a reaction with malonic ester [7], and similarly prepared the homologous dimethyl ester **22.** The diester **5** was converted by hydrolysis with decarboxylation to the monocarboxylic acid **23** [7]. Our attempts to convert the acid to its sodium salt were unsuccessful; mild treatment with sodium hydroxide, sodium bicarbonate, sodium alkoxide, or



Compound	X	Cpd	X
5	$C(CO_2C_2H_2)_2$	**50**	S
22	$C(CO_2CH_3)_2$	**51**	SO_2
23	$CHCO_2H$	**52**	$C(CN)_2$
24	NNH_2	**53**	NH
25	$NN{=}C(CH_3)_2$	**54**	$NCOCH_3$
49	NCH_2CH_2OH	**55**	$NCOCF_3$

sodium hydride gave intractable mixtures, in agreement with a known instability of the bimane nucleus toward alkali [6].

By replacing ammonia with hydrazine in Kosower's scheme for converting *syn*-(bromomethyl,methyl)bimane **17** to *μ*-amino-*syn*-(methylene, methyl)bimane **53** [7] the corresponding N-amino derivative **24** was obtained without competitive formation of the cyclic hydrazine isomer (with an eight-membered ring). The hydrazine **24** was characterized by conversion to its perchlorate salt and to the hydrazone derivative **25** obtained from acetone.

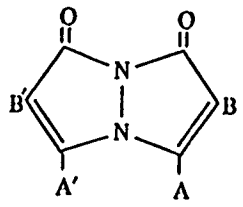
syn-(*Benzo*)- *and* syn-(*α-naphtho*)*bimanes* ***28*** *and* ***36***

Dehydrogenation of the previously reported *syn*-(tetramethylene)bimane (**26**) [6] by treatment with dichlorodicyanobenzoquine (DDQ) afforded both *syn*-(benzo)bimane **28** and the intermediate *syn*-(benzo,tetramethylene)bimane **27.** Attempted dehydrogenation of bimane **26** by treatment with either 1,4-chloranil or palladium (10%) on charcoal was unsuccessful.

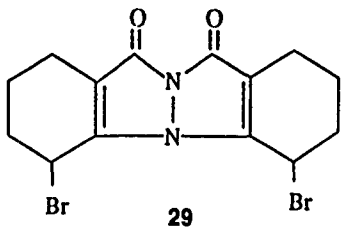
Bromination converted the bimane **26** to a dibromide that was given the tentative assignment of 4,6-dibromo-1,2,3,4,6,7,8,9-octahydro-10*H*,12*H*-indazolo[1,2-*a*]indazol-10,12-dione **29.** Treatment with an excess of DDQ converted the dibromide **29** to *syn*-(benzo)bimane **28.** The formation of a bromo derivative of bimane **28** was not detected.

An alternative approach to the preparation of *syn*-(benzo)bimane **28** that called for dehydration with cyclization of N,N-di-*o*-carboxyphenylhydrazine **32** was abandoned when the corresponding nitrosamine precursor **31** was not obtained by the treatment of di-*o*-carboxyphenylamine **30** [17] with nitrosating agents. A related conversion of N,N'-di-*o*-carboxyphenylhydrazine **33** [$(o\text{-}HO_2CC_6H_4NH)_2$] to *anti*-(benzo)bimane **34** was reported in 1916 [18].

syn-(*α*-Naphtho)bimane **36** was similarly obtained by a dehydrogenation of 5,6,10,-11-tetrahydro-7*H*,9*H*-benz[6,7]indazolo[1,2-*a*]benz[*g*]indazol-7,9-dione **35** by treatment with palladium (10%) on charcoal. The bimane **35** was prepared



Compound	A,B	A',B'
26	$(CH_2)_4$	$(CH_2)_4$
27	$(CH_2)_4$	$(CH)_4$
28	$(CH)_4$	$(CH)_4$
46	$HOCH_2$, CH_3	CH_3, CH_3
47	$CH_3CO_2CH_2$, CH_3	CH_3, CH_3



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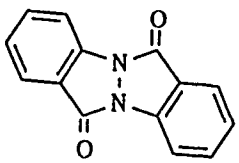
$(o\text{-}HO_2CC_6H_4)_2NX$

30 X = H
31 X = NO
32 X = NH_2



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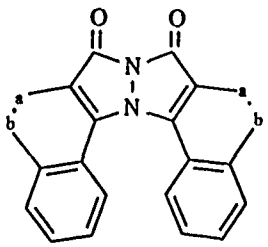
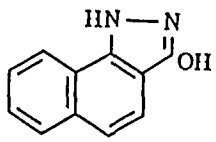


35 a · b = CH_2CH_2
36 a · b = CH=CH



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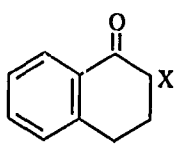
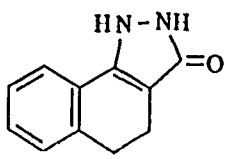


37 X = $CO_2C_2H_5$



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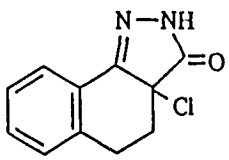

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from ethyl 1,2,3,4-tetrahydro-1-oxo-2-naphthoate **37** [19] by treatment with hydrazine to give 1,2,4,5-tetrahydro-3*H*-benz[*g*]indazol-3-one **38** followed by chlorination to give 3a-chloro-2,3a,4,5-tetrahydro-3*H*-benz[*g*]indazol-3-one **39** and treatment with potassium carbonate. A structure confirmation of the indazolone **38** was provided by its dehydrogenation over palladium to give 1*H*-benz[*g*]-indazol-3-ol **40.** In the absence of an x-ray crystallographic analysis, precluded by inability to obtain a crystalline modification, helicity for bimane **36** was corroborated by an analysis based on molecular modeling. In contrast to the *syn*-(benzo)bimane **28** in which the carbon atoms attached to the axial substitution sites are calculated to lie in the molecular plane, the corresponding carbon atoms in the *syn*-(α-naphtho)bimane **36** are calculated to be displaced by 0.53 Å above and below the mean molecular plane.

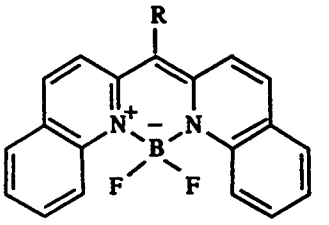
syn-*BIMANE LASER ACTIVITY*

Background Information

In water *syn*-(methyl,hydrogen)bimane **12** [6] showed fluoroescence λ_{max} 430 nm (Φ = 0.7), T-T absorption λ_{max} 490 nm with a shoulder at λ 420 nm, and no laser activity [20]. For comparison *syn*-(methyl,methyl)bimane **1** in water showed fluorescence λ_{max} 480 nm (Φ = 0.7), the same T-T absorption curve, and broad-band laser activity at λ 504 nm [5a]. It was suggested that a long-axis methyl substituent introduced a red shift solvatochromic effect on the fluorescence of the bimane **1** in water that promoted its laser activity above 500 nm where T-T absorption had steeply declined in intensity [5a]. The lasing efficiency (about 40% as efficient as coumarin 30) [21] was low—presumably a consequence of declining fluorescence intensity in the same spectral region [5a]. An absence of detectable laser activity from the bimane **1** in ethanol or in *p*-dioxane was attributed to solvatochromic shifts in fluorescence λ_{max} to 460 and 420 nm, respectively, where T-T absorption was more intense [5a]. Laser activity for *syn*-(hydrogen, methyl)bimane Type I (A = H, B = CH_3), fluorescence λ_{max} 460 nm (Φ = 0.6) [22], was not investigated; therefore a short-axis methyl substituent effect on laser activity was not directly established.

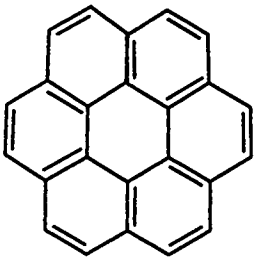
A study of the polarization of low energy electronic transitions (S-S and T-T) revealed the presence of two differently polarized T-T transitions in the spectral region of fluorescence for *syn*-bimanes. This increased the complexity of both long- and short-axis substituent effects on the T-T absorption and indirectly on the laser activity for *syn*-bimanes [20]. Investigations are planned to unravel these and other polarization effects in bimanes.

Angular *endo*-annelation was found in the laser active "boradiazinium salt" **41** [23] but was not



41 R = 2-isoquinolyl

extended to test the possibility of a helical laser dye. That helicity could create an interference with luminescence was shown in an examination of a series of hydrocarbons in which progressive helicity correlated with diminished fluorescent intensity [24]. Presumably laser activity in coronene **42** [25] was enhanced by chromophore planarity. We have herein reported the angular *endo*-annelation of *syn*-bimane into four-ring and six-ring systems.



42

RESULTS AND DISCUSSION

syn-Bimane derivatives offered a promising new source of laser dyes for the spectral region 500–530 nm. An examination of 18 Type I, two Type II, 13 Type III, and four annelated *syn*-bimanes revealed significant laser activity in eight from Types I and II (Table 1) and five from Type III (Table 2). Relative efficiencies, RE (± 10%), in laser power output were determined by comparison with the performance shown by a 7.5×10^{-4} M solution in ethanol of coumarin 30 (RE arbitrarily 100). Bimanes **3, 5, 18,** and **22** (Tables 1 and 2) gave RE > 80. Each of these four dyes offered a high quantum fluorescence yield ($\Phi > 0.7$), solvatochromic control of interference from absorption (S-S and T-T), superior photostability, and availability. In addition, dyes **3** and **18** were water soluble.

A replacement of the ester groups in dye **5** (or **22**) with cyano groups offered the strongly fluorescent μ-dicyanomethylene-*syn*-(methylene,methyl) bimane **52** (RE 0). A complete inhibition of laser activity in **52** was attributed in part to an electronic interaction between the cyano groups and the nearby chromophore. (In other examples inhibition of luminescence was attributed to a similar interaction between nitro and chromophore

TABLE 1 *syn*-(A,B)Bimanes, Type I and *syn*(A,B)(A′,B′)Bimanes, Type II: Laser Activity in the Region 500–530 nm

Compound[a,b]				Power Output, P_1 and P_2 (mJ)			
No.	A	B	Solvent[c]	P_1[d]	RE[c] (%)[e]	P_2[f]	RE (%)[e]
1	CH_3	CH_3	HFI	2.45	41	5.27	43
2	CH_3	Cl	TFE	1.75	29	5.15	42
3	$CH_3CO_2CH_2$	CH_3	H_2O	4.37	72	10.92	89
4	FCH_2	CH_3	TFE[g,h]	0.31	5	3.0	24
18	$(CH_3O)_2P(O)CH_2$	CH_3	H_2O[i]	4.43	73	10.43	85
20	$HOCH_2$	CH_3	H_2O	3.48	58	8.19	67
No.	*A,B*	*A′B′*					
26	$(CH_2)_4$	$(CH_2)_4$	TFE[j]	0.70	12	2.60	21
46[k]	$HOCH_2$, CH_3	CH_3, CH_3	HFI[m]	0.23	4	2.39	19
47	$CH_3CO_2CH_2$, CH_3	CH_3, CH_3	H_2O[n]	0.7	15	4.98	56

[a] 10^{-3} M.
[b] Fluorescence in the region 435–460 nm with Φ values in the range 0.6–0.9 was reported for compounds *1* [6], *2* [6], *3* [8], *4* [5c], *20* [8], *26* [6], and *46* [7]. See Experimental for compound *18*.
[c] HFI, hexafluoroisopropanol; TFE, trifluoroethanol.
[d] Dye pumped to 5.0 J.
[e] Relative efficiency compared to 100 (arbitrary) for coumarin 30.
[f] Dye pumped to 10.0 J.
[g] Mixed with water (10%).
[h] Laser activity at 435 nm from bimane **4** in dioxane.
[i] Laser activity at 438 nm from bimane **18** in dioxane.
[j] Mixed with water (10%).
[k] Rapid photodecomposition.
[m] Concentration not determined.
[n] 20% HFI.

TABLE 2 μ-X-*syn*-(Methylene,methyl)bimanes, Type III: Laser Activity in the Region 500–530 nm

Compound[a,b]			Power Output, P_1 and P_2 (mJ)			
No.	X	Solvent[c]	P_1[d]	RE(%)[e]	P_2[f]	RE(%)[e]
5	$C(CO_2C_2H_5)_2$	HFI	4.76	79	10.00	82
22[h]	$C(CO_2CH_3)_2$	TFE[g]	5.85	97	13.13	107
24	NNH_2	H_2O[i]	2.17	36	6.27	51
50	S	HFI	2.98	49	7.55	61
52	$C(CN)_2$	H_2O[j]	0.17	3	0.4	3
53	NH	H_2O	0	0	1.22	9
55	$NCOCF_3$	TFE[g]	0.33	5	1.6	13

[a] 10^{-3} M.
[b] Fluorescence, λ (Φ): 426 (0.8) for compound **5** and 447 (0.8) for compound **50** were reported [7]. See Experimental for compounds **22**, **24**, and **55**.
[c] HFI, hexafluoroisopropanol; TFE, trifluoroethanol.
[d] Dye pumped to 5.0 J.
[e] Relative efficiency compared to 100 (arbitrary) for coumarin 30.
[f] Dye pumped to 10.0 J.
[g] Mixed with water (10%).
[h] Ref. 7.
[i] Contained perchloric acid. An aqueous solution of the perchlorate salt (Experimental) in water gave no laser activity when pumped to 5.0 J and 0.43 mJ (RE 3.5%) when pumped to 10.0 J.
[j] Mixed with 20% HFI.

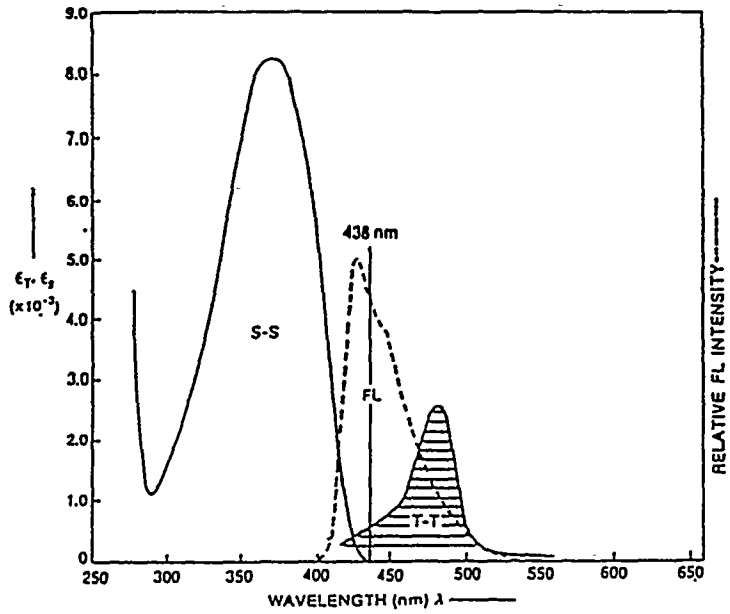


FIGURE 1 Absorption (S-S and T-T), fluorescence (FL), and the center of broad-band laser activity at 438 nm for *syn*-(dimethoxyphosphinylmethyl,methyl)bimane **18** in *p*-dioxane. The T-T absorption spectrum was recorded at 77°K, employing a 2×10^{-4} molar solution of 2-methyltetrahydrofuran. The S-S and Fl (1×10^{-3} molar) spectra were recorded with *p*-dioxane as solvent.

groups. [3].) The conspicuous absence of a cyano derivative in current lists of dyes [2–4] was taken an an indication that the cyano group within the dye molecule generally quenched laser activity.

The diphosphonate **18** was noted for a solvatochromic effect that shifted its fluorescence maximum from 425 nm in dioxane to 460 nm in water without shifting T-T absorption at about 480 nm to afford laser activity at 438 nm in one and at 514 nm in the other solvent (Figures 1 and 2). In water the solubility of the diphosphonate **18** (0.2 M) surpassed coumarin 30 (less than 10^{-4} M) but was 20% less power efficient (Figure 3) when each was pumped to 4.5 J. The diphosphonate **18** showed good photostability; however, after exposure in methanol to irradiation at 250 nm for 1 week it was completely converted to unidentified material. Under similar prolonged irradiation *syn*-(methyl, methyl)bimane **1**, a yellow solid, was converted to an unknown colorless powder.

Dyes that showed RE 20-80 included the bimanes **1** [5a], **2** [5b], **4** [5b], **20**, and **26** (Table 1); and bimanes **24** and **50** (Table 2). A long-axis alkyl substituent effect that was discovered for the methyl group in bimane **1** [5a] was greatly diminished in *syn*-(tetramethylene)bimane **26** and was ineffective in bimanes **6–9** that were laser inactive. The performance (RE 42) that was characteristic of *syn*-(methyl,chloro)bimane **2**, Φ 0.8 (Table 1) was not shared with *syn*-(carboethyoxy,chloro)bimane **45**, Φ 0.1, (inactive) and *syn*-(phenyl,chloro)bimane **44**, Φ 0.6, (inactive). Although these results are in line with the general requirement for the presence of strong fluorescence, the laser inactivity in the latter example was attributed in part to interference from an assumed T-T absorption (phenyl group).

The results obtained from *syn*-(hydroxymethyl,methyl)bimane **20**, Φ 0.60, (RE 67) and *syn*-(hydroxymethyl,methyl)(methyl,methyl)bimane **46**, Φ

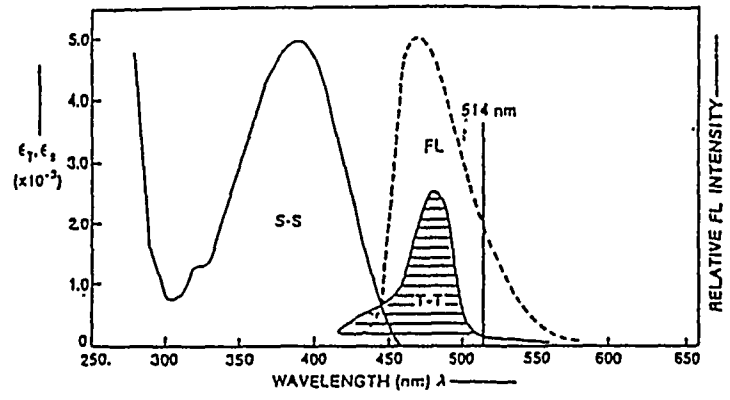


FIGURE 2 Absorption (S-S and T-T), fluorescence (FL), and the center of broad-band laser activity at 514 nm for *syn*-(dimethoxyphosphinylmethyl,methyl)bimane **18**. The T-T absorption spectrum was recorded at 77°K, employing a 2×10^{-4} molar solution of 2-methyltetrahydrofuran. The S-S and Fl (1×10^{-3}) spectra were recorded with water as a solvent.

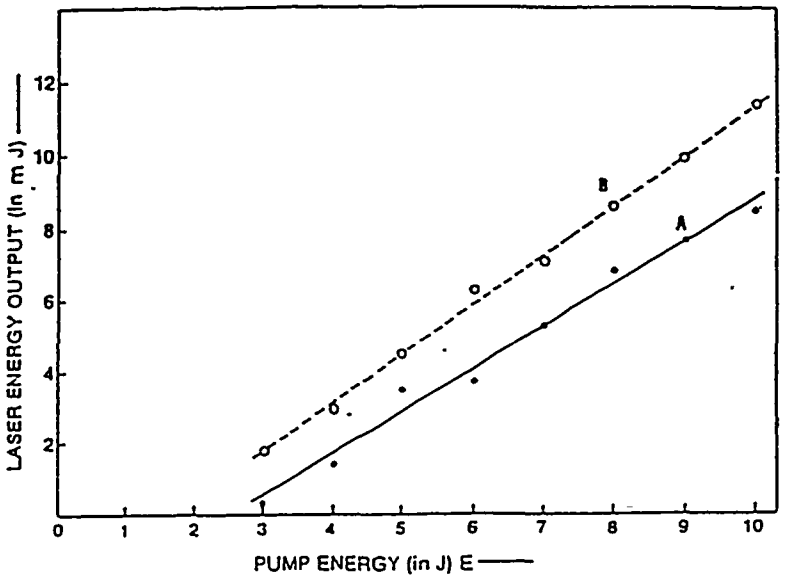


FIGURE 3 Laser energy output (mJ) as a function of flashlamp pump energy (J) of (A) *syn*-(dimethoxyphosphinylmethyl,methyl)bimane **18**, 1×10^{-3} M in water and (B) coumarin 30, 7.5×10^{-4} M ethanol.

0.80, (RF. 19) (Table 1) appeared to be in conflict; however, a decrease in the laser activity of the alcohol **46** was attributed to its rapid photodecomposition, a property not shared with the other bimanes in this report. Although a lower performance rating for the glycol **20** (RE 67), relative to its diacetate ester **3** (RE 89), could be attributed to self-quenching brought about by dye aggregation as a result of hydrogen bonding, a parallel improvement in the performance of the alcohol **46** (RE 19) on conversion to its acetate ester **47** (RE < 19) was not observed.

Our results indicated that bimane laser dyes with μ-heteroatom bridges did not afford superior performances. No laser activity was detected from μ-amino-*syn*-(methylene,methyl)bimane **53**, its N-β-hydroxyethyl derivative **49**, and its N-acetyl derivative **54**. The N-trifluoroacetyl derivative **55** (RE 13) and the N-amino derivative **24** (RE 51) (Table 2) showed weak laser activity. There was some improvement shown by μ-thia-*syn*-(methylene,methyl)bimane **50** (RE 61); however, μ-sulfono-*syn*-(methylene,methyl)bimane **51** was laser inactive. Laser inhibition as a result of an electronic interaction between amino, thia, or sulfono bridges and the nearby chromophore was assumed.

Strong T-T absorption for *syn*-(benzo)bimane **28** was shown to interfere throughout the fluorescence spectral region [20] and presumably quenched laser activity. A similar quenching effect was assumed for the related bimanes **27** and **35**. The absence of laser activity in bimanes **17, 29, 44,** and **45** was partially attributed to the heavy atom effect. A low fluorescence quantum yield, Φ 0.1, for laser inactive *syn*-(α-naphtho)bimane **36** (compare Φ 0.9 for *syn*-(benzo)bimane **28**) was attributed to further disruption in the planarity of the bimane chromophore that was presumably brought about by helicity.

EXPERIMENTAL

Spectral data were obtained from the following instruments: Pye–Unicam SP 200 IR, Varian A-60 and JEOL FX Q NMR, Hewlett-Packard 5985 (70 eV) (GC-MS), Beckman DU (UV), and a Perkin-Elmer LS-5B Luminescence Spectrometer. A dye laser was constructed at the Naval Ocean Systems Center [26]. It operated in the nonflowing (static) mode and had no tuning capability. The dye cell (2.5 mm diam., 50 mm long) had an elliptical cavity configuration of small eccentricity. The flashlamp pulser, EG & G model FX 139C-2, had a rise time of 200 ns, half-width length of 600 ns, and input energy of 2 J at 6.32 kV, 5 J at 10.00 kV, 7.2 J at 12.00 kV, and 10 J at 14.14 kV [5a]. Laser energy outputs were measured with an accuracy of ±5% by a Scientech 365 power and energy meter [5c]. Laser activities are described in Tables 1 and 2.

For each product the IR spectrum agreed with the literature data and/or supported the assigned structure. Each recorded UV absorption was restricted to the highest wavelength. H NMR (60 MHz) spectra were run in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR were recorded at 22.5 MHz with the deuterated solvent as an internal reference. The central peak of the solvent multiplet signal was assigned: δ 77.00 ($CDCl_3$), 39.50 $(CD_3)_2(SO)$. Fluorescence quantum yields were determined by reference to *syn*-(methyl, methyl)bimane **1**, Φ 0.72 [6], *syn*-(benzo)bimane **28**, Φ 0.9 [27], and/or quinine sulfate, Φ 0.55. The latter reference was abandoned for several determinations when it led to erratic results. The mass spec-

tra were electron impact (70 eV). Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. Elemental analyses were obtained from Midwest Micro Lab, Indianapolis, IN, and Galbraith Laboratories, Knoxville, TN. Solvents were removed by rotary evaporation under reduced pressure unless indicated otherwise. Column chromatography was performed on silica gel (various grades). Triplet extinction coefficients over the laser action spectral region of the dye were measured at the temperature of liquid nitrogen by equipment previously described [28] using McClure's method [29]. Molecular mechanics calculations were performed on a MicroVAX 2000 computer with Evans and Sutherland PS390 graphics display using the BIOGRAF [30] software package. The force field parameters were taken from the MM2 set [31].

Solvents, reagents, and starting materials that were obtained from the Aldrich Chemical Company, Milwaukee, WI included acetic anhydride, acetone, acetonitrile, acryloyl chloride, alumina, ammonium chloride, benzaldehyde, benzene, bromine, β-bromoethyl acetate, carbon tetrachloride, celite, cetyltrimethylammonium Bromide *m*-chloroperbenzoic acid, chloroform-d, dichlorodicyanobenzoquinone (DDQ), dichloromethane, diethyl acetylsuccinate, diethyl carbonate, diethyl ethoxymethylenemalonate, N,N-disopropylethylamine, N,N-dimethylformamide (DMF), dimethyl sulfoxide-d_6 (DMSO-d_6), *p*-dioxane, 18-crown-6-ether, ethanol, ethyl acetate, ethyl benzylacetoacetate, hexane, hexafluoroisopropanol, hydrazine hydrate, iodobenzene diacetate, isopropanol, methanol, α-methyltetrahydrofuran, nitric acid, palladium (10% on charcoal), perchloric acid, peroxytrifluoroacetic acid, petroleum ether, potassium bromide, potassium *tert*-butoxide, potassium carbonate, potassium fluoride, potassium superoxide, silica gel (230–400 mesh, 60 Å), sodium bicarbonate, sodium hydride, sodium hydroxide, sodium sulfate, tetrahydrofuran (THF), α-tetralone, *p*-toluenesulfonic acid, triethylamine, trifluoroacetic anhydride, trifluoroethanol, and trimethyl phosphite. Coumarins 6, 30, 120, and 314, rhodamine 6G, sulforhodamine B and thin layer chromatography sheets were obtained from Eastman Kodak Co., Rochester, NY. Chlorine was obtained from Matheson Gas Products, Secaucus, NJ. Nitrogen was obtained from Air Products and Chemicals, Allentown, PA. Hydrogen peroxide (90%) was obtained from Shell Chemical Company, Houston, TX.

The following compounds were prepared according to the directions cited: bimanes type I: *syn*-(A,B)bimanes where (A,B) was (methyl,hydrogen) in **12** [6], (methyl,methyl) in **1** [6], (bromomethyl,methyl) in **17** [6, 8], (hydroxymethyl,methyl) in **20** [8], (tetramethylene) in **26** [6], (methyl,phenyl) in **43** [6], (phenyl,chloro) in **44** [6], and (carboethoxy,chloro) in **45** [22]; bimanes type II: *syn*-(hydroxymethyl,methyl)(methyl,methyl)bimane **46** [6]; bimanes type III: μ-X-*syn*-(methylene, methyl)bimanes where X was dicarboethoxymethylene in **5** [7], dicarbomethoxymethylene in **22** [7], carboxymethylene in **23** [7], thia in **50** [7], sulfono in **51** [7], dicyanomethylene in **52** [7], amino in **53** [7], and acetylamino in **54** [7]; bimanes type IV: *anti*-(methyl,hydrogen)bimane **13** [6] and *anti*-(amino,hydrogen)bimane **11** [13]; miscellaneous: 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one **10c** [32], 4-β-acetoxyethylethyl-3-methyl-2-pyrazolin-5-one [33], and ethyl 1,2,3,4-tetrahydro-1-oxo-2-naphthoate **37** [19].

4-Benzyl-4-chloro-3-methyl-2-pyrazolin-5-one ***10b***

Hydrazine hydrate (10.5 g, 0.21 mol) in methanol (20 mL) was added slowly with stirring to ethyl benzylacetoacetate (44.0 g, 0.2 mol) in methanol (200 mL). The mixture was heated at 65°C for 1 h and cooled to bring about the precipitation of 3-methyl-4-benzyl-2-pyrazolin-5-one that recrystallized from ethanol as a colorless solid, 32.0 g (85%), mp 230–231°C (lit. [34] 232°C); H NMR ($CDCl_3$): δ 2.0 (s, 3 H, CH_3), 3.6 (s, 2 H, CH_2), and 7.2 (s, 5 H, C_6H_5). A solution of the pyrazolinone (32.0 g, 0.17 mol) in dichloromethane (300 mL) was treated with a stream of chlorine gas until the solid phase disappeared and the solution became yellow. Traces of chlorine were removed by purging with a stream of nitrogen. The solvent was removed to leave a yellow oil that recrystallized from benzene to give the chloropyrazolinone **10b** as a yellow solid, 32.5 g (86%); mp 75–76°C; H NMR ($CDCl_3$): δ 2.1 (s, 3 H, CH_3), 3.3 (d, 2 H, CH_2), 7.2 (s, 5 H, C_6H_5), 8.9 (broad, 1 H, NH). Anal. calcd for $C_9H_{11}N_2OCl$: C, 59.32; H, 4.94; N, 12.58;. Cl, 15.95. Found: C, 59.26; H, 5.08;. N, 12.79; Cl, 15.90.

syn-(*Methyl,benzyl*)*bimane* ***6***

The prepared mixture (10 g) of potassium fluoride and neutral alumina (2 : 3 by wt) was added to the chloropyrazolinone **10b** (1.0 g, 5 mmol) in dichloromethane (100 mL) at 10°C and the mixture was stirred for 1 h. Filtration and concentration of the mother liquor left a residue that recrystallized from carbon tetrachloride to give the bimane **6** as a yellow crystalline solid, 0.5 g (62%); mp 124–125°C; H NMR ($CDCl_3$): δ 2.25 (s, 6 H, CH_3), 3.6 (s, 4 H, CH_2), 7.25 (s, 10 H, C_6H_5); ^{13}C NMR ($CDCl_3$): δ 159.78 (CO); 145.99 (0=C—C=**C**); 138.58, 128.43, 128.04, and 126.22 (C_6H_5); 115.56 (0=C-**C**=C); 27.51 (CH_2); 11.71 (CH_3). UV (CH_3CN): λ (ε) 375 (7916); fluorescence (dioxane): λ (Φ) 417 (0.8); EI-MS: 344 (M^+). Anal. calcd for $C_{22}H_{20}N_2O_2$: C, 76.74; H, 5.81; N, 8.13. Found: C, 76.52; H, 5.80; N, 8.25.

When the reaction was catalyzed by potassium

carbonate a mixture (1 : 1) (87%) of the bimane **6** and its *anti* isomer **A6** was obtained.

syn-(*Methyl,carboethoxymethyl*)*bimane* **7**

To 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one (4.4 g, 20 mmol) in dichloromethane (200 mL) a prepared mixture (44 g) of potassium fluoride and neutral alumina (2 : 3 by wt) was added at 25°C with stirring that was continued for 1 h. After filtration the mother liquor was concentrated to leave a brown solid that was purified by flash chromatography from a column of silica gel (dichloromethane) to give *anti*-(methyl,carboethoxymethyl)bimane **A7** as a colorless solid, 1.2 g (36%), mp 183–184°C (lit. [32] mp 180°C), followed by the *syn* isomer **7** as a pale-yellow solid, 0.5 g (15%); mp 146–147°C; H NMR ($CDCl_3$): δ 1.27 (t, 6 H, CH_3), 2.4 (s, 6 H, CH_3), 3.3 (s, 4 H, CH_2), 4.13 (q, 4 H, CH_2); UV (CH_3CN): λ (ε) 370 (7303); fluorescence (ethanol): λ (Φ) 420 (0.8); EI-MS: 336 (M^+). Anal. calcd for $C_{16}H_{20}N_2O_6$: C, 57.14; H, 5.92; N, 8.33. Found: C, 56.91; H, 5.71; N, 8.58. When an attempt to repeat the preparation with potassium carbonate as the catalyst was made the starting material was partially converted to a mixture of bimanes **3** and **A3** after 20 h at 25°C.

4-β-Acetoxyethyl-4-chloro-3-methyl-2-pyrazolin-5-one ***10d***

Chlorine gas was bubbled into a suspension of 4-β-acetoxyethyl-3-methyl-2-pyrazolin-5-one (15.0 g, 80 mmol) in dichloromethane (500 mL) until the suspension dissolved to give a yellow solution. The solution was stirred for an additional 30 minutes. Excess chlorine and the solvent were removed under reduced pressure to give a yellow residue, which was recrystallized from a mixture of hexane and carbon tetrachloride to give 4-β-acetoxyethyl-4-chloro-3-methyl-2-pyrazolin-5-one **10d** as a colorless crystalline solid, 13.5 g (76%); mp 94–95°C; H NMR ($CDCl_3$): δ 2.00 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.47 (t, 2 H, CH_2), 4.05 (t, 2 H, CH_2), 9.35 (br, 1 H, NH). Anal. calcd for $C_8H_{11}N_2O_3Cl$: C, 43.95; H, 5.07; N, 12.81; Cl, 16.22. Found: C, 43.83; H, 5.04; N, 12.89; Cl, 16.66.

syn-(*Methyl, β-acetoxyethyl*)*bimane* ***8***

4-β-Acetoxyethyl-4-chloro-3-methyl-2-pyrazolin-5-one **10d** (5.0 g, 23 mmol), potassium carbonate (10.0 g, 72 mmol), and water (2 mL) were added to dichloromethane (300 mL). The resulting suspension was stirred vigorously for 4 h. The reaction was monitored with thin-layer chromatography (ethyl acetate). Celite 545 (10 g) was then added, and the resulting mixture was passed through a short silica gel column (dichloromethane, 100 mL). The solvent was removed to give a yellow residue which was recrystallized from ethyl acetate to give 2.7 g (70%) of the bimane **8**, mp 134–135°C; H NMR ($CDCl_3$): δ 2.03 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.62 (t, 2 H, CH_2), 4.15 (t, 2 H, CH_2); UV (H_2O): λ (ε) 384 (6048); fluorescence (dioxane): λ (Φ) 457 (0.8). Anal. calcd for $C_{16}H_{20}N_2O_6$: C, 57.13; H, 6.39; N, 11.10. Found: C, 57.08; H, 6.57; N, 10.99.

syn-(*Methyl,2-hydroxyethyl*)*bimane* ***9***

syn-(Methyl,acetoxyethyl)bimane **8** (1.0 g, 3 mmol) and toluenesulfonic acid (20 mg) was dissolved in methanol (50 mL). The solution was heated at 60°C for 2 days, and the reaction was monitored with thin-layer chromatography (ethyl acetate). The solvent was removed to give a yellow residue which recrystallized in acetonitrile and dimethylformamide to give 0.30 g (40%) of the bimane **9** mp 186.5–188°C; H NMR ($CDCl_3$-DMSO-d_6): δ 2.33 (t, 2 H, CH_2) 2.39 (s, 3 H, CH_3), 3.39 (t, 2 H, CH_2), 3.77 (br, 1 H, OH); UV (H_2O): λ (ε) 317 (23,048); fluorescence (dioxane): λ (Φ) 464 (0.5). Anal. calcd for $C_{12}H_{16}N_2O_4$: C, 57.13; H, 6.39; N, 11.10. Found: C, 57.08; H, 6.57; N, 10.99.

Ethyl 4-chloro-5-oxo-2-pyrazoline-4-carboxylate ***10e***

Hydrazine hydrate (5.5 g, 0.1 mol) in ethanol (20 mL) was added with stirring to a solution of diethyl ethoxymethylenemalonate (21.6 g, 0.1 mol) in ethanol (200 mL). The mixture was heated at 80°C for 18 h and cooled. Ethyl 2-pyrazolin-5-one-4-carboxylate precipitated and recrystallized from ethanol as a colorless crystalline solid, 7.5 g (48%); mp 177–178°C (dec); H NMR (DMSO- d_6): δ 1.2 (t, 3 H, CH_3), 4.2 (q, 2 H, CH_2), 7.9 (s, 1 H, CH); EI-MS: 156 (M^+). Anal. calcd for $C_6H_8N_2O_3$: C, 46.15; H, 5.12; N. 17.94. Found: C, 46.25; H, 5.13; N, 17.93. The pyrazolinone (5.0 g, 32 mmol) in dichloromethane (200 mL) was treated with a stream of chlorine gas at 25°C until the solid phase disappeared and the solution became yellow. Excess chlorine was purged with a stream of nitrogen. Removal of the solvent left the chloropyrazolinone **10e** or an isomer that recrystallized from benzene as a yellow solid, 5.5 g (90%); mp 103–105°C; H NMR ($CDCl_3$): δ 1.3 (t, 3 H, CH_3), 4.4 (q, 2 H, CH_2), 7.4 (s, 1 H, CH), and 9.6 (broad, 1 H, CH). Anal. calcd for $C_6H_7N_2O_3Cl$: C, 37.79; H, 3.79; N, 14.69; Cl, 18.68. Found: C, 37.87; H, 3.57; N, 14.63; Cl, 18.72. Attempts to convert the product **10e** (or isomer) under the catalysis of either potassium carbonate, or N,N-diisopropylethylamine, or potassium fluoride on alumina, or sodium hydride in tetrahydrofuran to *syn*-(hydrogen,carboethoxy)bimane were unsuccessful.

anti-(*Methyl,nitro*)(*methyl,hydrogen*)*bimane* **16**

After a mixture of nitric acid (90%, 0.20 mL) and acetic anhydride (0.75 mL) was stirred at 0°C for 15 m, *anti*-(methyl,hydrogen)bimane **13** (0.16 g, 1.0 mmol) was added slowly. The mixture was stirred at 0°C for 30 m and poured onto crushed ice to precipitate the nitrobimane **16** as an orange solid, 0.12 g (57%), mp 196°C (dec) (acetone). H NMR ($CDCl_3$): δ 2.6 (s, 3 H, CH_3), 3.0 (s, 3 H, CH_3), and 5.5 (s, 1 H, CH); EI-MS: 209 (M^+). Anal. calcd for $C_8H_7N_3O_4$: C, 45.94; H, 3.37; N, 20.09. Found: C, 45.62; H, 3.19; N, 19.59.

Attempts to extend the nitration reaction to *syn*-(methyl,hydrogen)bimane **12** gave intractable mixtures. A trace amount of solid was thought to be a *syn*-isomer of bimane **16** since the mass spectrometric analysis showed EI-MS 209 (M^+).

anti-(*Amino,nitro*)*bimane* **15**

Following the above procedure *anti*-(amino,hydrogen)bimane **11** (0.4 g, 2.4 mmol) in a mixture of nitric acid (90%, 0.7 mL) and acetic anhydride (2.0 mL) at 0°C with stirring for 30 min gave the dinitrobimane **15** as a red orange solid, 0.56 g (91%), mp 318°C (dec) (acetone). ^{13}C NMR (DMSO-d_6): δ 107.8, 151.3, and 153.7; EI-MS 256 (M^+). Anal. calcd for $C_6H_4N_6O_6$: C, 28.13; H, 1.56; N, 32.81. Found: C, 28.07; H, 1.57;. N, 32.07.

Oxidation of Aminobimanes

The diaminobimane **11** in a mixture of trifluoroacetic anhydride and hydrogen peroxide (90%) was converted to an intractable yellow gum. The diaminodinitrobimane **15** was unaffected by *m*-chloroperbenzoic acid, or peroxytrifluoroacetic acid, or iodobenzene diacetate.

A slurry of the diaminodinitrobimane **15** (0.8 g, 3.1 mmol), 18-crown-6 ether (0.15 g), and potassium superoxide (1.0 gm 14.1 mmol) in benzene was stirred for 17 h at 25°C under nitrogen. Addition of water gave a clear yellow aqueous layer that was acidified (dilute hydrochloric acid) to precipitate a trace amount of solid, mp > 300°C, that was discarded. Addition of ethanol to the filtrate caused the precipitation of a potassium salt as a colorless solid, 0.15 g (13%), mp 150°C (dec) (aqueous ethanol). Anal. calcd for $C_6N_4O_8K_2 \cdot 1.5\ H_2O$: C, 19.94; H, 0.83; N, 15.51. Found: C, 19.82; H, 0.71; N, 15.96.

syn-(*Dimethoxyphosphinylmethyl,methyl*) *bimane* **18**

A mixture of *syn*-(bromomethyl,methyl)bimane **17** (7.0 g, 0.2 mmol) and trimethyl phosphite (10 mL) was heated at 115°C for 30 m as it became homogeneous and solidified. After trituration with hexane (50 mL) the mixture was taken up in ethyl acetate. The bimane **18** separated as a yellow crystalline solid, 6.3 g (78%); mp 224–225°C; H NMR ($CDCl_3$): δ 1.87 (d, 6 H, J = 4 Hz, CH_3), 3.72 (d, 4 H, J = 22 Hz, CH_2), 3.75 (d, 12 H, J = 10 Hz, OCH_3); ^{13}C NMR ($CDCl_3$): δ 159.52 (CO), 140.40 and 139.95 (O=C—C=**C**), 114.91 and 114.58 (O=C—**C**), 53.52 and 53.19 (PO-CH_3), 26.34 and 20.09 (CH_2), and 6.83 (CH_3); UV (CH_3CN): λ (ε) 380 (6984); fluorescence (dioxane): λ (Φ) 417 (0.7); EI-MS: 408 (M^+). Anal. calcd for $C_{14}H_{22}N_2O_8P_2$: C, 41.17; H, 5.39; N, 6.86; P, 15.19. Found: C, 40.95; H, 5.35; N, 6.80; P, 15.41.

syn-(*Styryl,methyl*)*bimane* **19**

A mixture of the diphosphonate **18** (1.0 g, 2.5 mmol), potassium carbonate (1.4 g, 10 mmol), benzaldehyde (0.5 g, 5 mmol), and water (2 mL) was heated at 100°C for 4 h, cooled, combined with dichloromethane (200 mL), and washed with water (2 × 50 mL). The organic layer was dried (sodium sulfate) and concentrated to leave a brown solid that recrystallized from methanol to give the bimane **19** as a yellow crystalline solid, 0.3 g (29%); mp 214–215°C; H NMR (DMSO-d_6): δ 2.1 (s, 6 H, CH_3), 7.3–7.8 (m, 14 H, C_6H_5CH=CH); ^{13}C NMR (DMSO-d_6): δ 161.36 (CO); 149.92 (O=C—C=**C**); 140.68 (C_6H_5**C**=C), 114.67 and 112.50 (C_6H_5C=**C**—C=**C**—C=O); 135.09, 129.68, 128.72, and 127.42 (C_6H_5); 8.02 (CH_3); UV (CH_3CN): λ (ε) 400 (2530); fluorescence (dioxane): λ (Φ) 428 (0.2); EI-MS: 368 (M^+). Anal. calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60. Found: C, 78.01; H, 5.52; N, 7.53.

To a slurry of potassium t-butoxide (0.8 g, 7.8 mmol) in N,N-dimethylformamide (DMF) (100 mL) the diphosphonate **18** (1.0 g, 2.5 mmol) in DMF (25 mL) was added with stirring under nitrogen at 25°C over a period of 2 h, heated at 70°C for 3 h, cooled, and treated with saturated aqueous ammonium chloride (10 mL). DMF was removed by distillation. The residue was treated with dichloromethane (200 mL), washed with water (2 × 50 mL), dried (sodium sulfate), and concentrated to give a brown solid that afforded the bimane **19** as a yellow crystalline solid, 0.22 g (25%), mp 214–215°C, after purification from methanol.

syn-(*Acryloxymethylene,methyl*)*bimane* **21**

Triethylamine (3.6 g, 36 mmol) and acryloyl chloride (3.4 g, 36 mmol) were added separately to *syn*-(hydroxymethyl,methyl)bimane **20** (2.0 g, 9 mmol) in DMF (50 mL) with stirring at 25°C over a period of 48 h. The mixture was combined with water (200 mL), extracted with chloroform (3 × 100 mL), washed with aqueous sodium bicarbonate (5%) (30 mL), dried (sodium sulfate), and concentrated to leave a dark brown solid. Purification by flash chromatographic separation from a column of silica gel (80 g, chloroform) gave the bimane **21** as a yellow

solid, 0.65 g (22%); mp 121–122°C; H NMR ($CDCl_3$): δ 1.9 (s, 6 H, CH_3), 5.2 (s, 4 H, OCH_2), and 5.8–6.6 (m, 6 H, CH_2=CH); UV (CH_3CN): λ (ε) 385 (7552); fluorescence (dioxane): λ (Φ) 432 (0.6); EI-MS: 332 (M^+). Anal. calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.81; N, 8.43. Found: C, 57.38; H, 4.79; N, 8.07.

syn-(*Acetoxymethyl,methyl*)(*methyl,methyl*) *bimane* **47**

Bromine (1.25 g, 7.8 mmol) in dichloromethane (25 mL) was added dropwise to *syn*-(methyl,methyl)bimane (1.5 g, 7.8 mmol) in dichloromethane (50 mL) at 25°C over a period of 1 h. The solution was stirred for 30 min, and the solvent was removed to leave a red residue that was dissolved in dichloromethane (40 mL). The solution was mixed with aqueous potassium acetate (2 M, 30 mL) that contained cetyltrimethylammonium bromide (300 mg) and stirred for 18 h in the dark. The organic layer was separated, washed with water, and dried (anhydrous sodium sulfate). The solvent was then removed, and the yellow residue gave 0.78 g (40%) of *syn*-(acetoxymethyl,methyl)(methyl,methyl)bimane as a yellow crystalline solid: mp 185–186.5°C (ethyl acetate); H NMR ($CDCl_3$) δ 1.82 (s, 3 H, CH_3), 1.94 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 5.04 (s, 2 H, CH_2); UV (dioxane): λ (ε) 373 (6836). Anal. calcd for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.19. Found: C, 57.31; H, 5.63; N, 11.38.

μ-Aminoimino-syn(*methylene,methyl*)*bimane* **24**

Hydrazine hydrate (0.5 g, 10 mmol) in acetonitrile (10 mL) was added to a solution of *syn*-(bromomethyl,methyl)bimane **17** (0.7 g, 2 mmol) in acetonitrile (25 mL) with stirring at 25°C. The reaction mixture contained a colorless precipitate after 10 m that was collected by filtration after the mixture was diluted with water. The precipitate was triturated with acetonitrile and dried and recrystallized from DMF to give the hydrazine **24** as a yellow solid, 0.3 g (68%); mp 220–221°C (dec); H NMR (trifluoroacetic acid): δ 1.8 (s, 6 H, CH_3), 4.5 (s, 4 H, CH_2); ^{13}C NMR (trifluoroacetic acid): δ 165.70 (CO), 148.50 (O=CC=**C**), 116.6 (0=C—**C**=C), 48.3 (CH_2), 5.4 (CH_3); UV (CH_3CN): λ (ε) 335 (5700); fluorescence(dioxane): λ (Φ): 419 (0.1); EI-MS: 220 (M^+). Anal. calcd for $C_{10}H_{12}N_4O_2$: C, 54.54; H, 5.45, N, 25.45. Found: C, 54.33; H, 5.48; N, 25.33. The monoperchlorate derivative was prepared in ethanol as a yellow solid, 85%, mp 182–183°C (dec); H NMR (D_2O): δ 1.8 (s, 6 H, CH_3), 4.03 (s, 4 H, CH_2); UV (H_2O): λ (ε) 339 (4611); fluorescence (water): λ (Φ) 460 (0.1); EI-MS: 220 (M^+-$HClO_4$). Anal. calcd for $C_{10}H_{13}N_4O_6Cl \cdot 1.5\ H_2O$: C, 34.53; H, 3.74; N, 16.14; Cl, 10.21. Found: C, 34.59; H, 4.28; N, 16.28; Cl, 10.41.

The hydrazine **24** combined with acetone to give the hydrazone **25** (85%); mp 182–183°C; H NMR ($CDCl_3$): δ 1.8 (s, 6 H, CH_3), 2.0 [d, 6 H, $C(CH_3)_2$], 3.8 (s, 4 H, CH_2); UV (CH_3CN): λ (ε) 339 (6932); fluorescence (dioxane): λ (Φ): 420 (0.15); EI-MS: 260 (M^+). Anal. calcd for $C_{13}H_{16}N_4O_2$: C, 60.00; H, 6.15; N, 21.53. Found: C, 59.85; H, 6.09; N, 21.46.

N-Trifluoroacetyl *μ-amino*-syn-(*methylene,methyl*)*bimane* ***55***

A suspension of *μ*-amino-*syn*-(methylene,methyl) bimane **53** (0.50 g, 2.4 mmol) in trifluoroacetic anhydride (7 mL) was stirred at 25°C for 2 h as a pale yellow precipitate appeared. The solvent was removed and the yellow residue recrystallized from a mixture of ethyl acetate and acetonitrile (1 : 1, 10 mL) to give the amide **55** as a colorless crystalline solid (0.30 g, 42%): mp 173–174°C; H NMR ($CDCl_3$) δ 1.86 (s, 3 H, CH_3), 4.78 (s, 2 H, CH_2); UV (CH_3CN): 331 nm (ε 6309); fluorescence (dioxane): λ (Φ) 418 (0.8); EI-MS: 301 (M^+). Anal. calcd for $C_{12}H_{10}N_3O_3F_3$: C, 47.85; H, 3.35; N, 13.95; F, 18.92. Found: C, 47.74; H, 3.34; N, 13.89; F, 18.73.

syn-*Benzobimane* ***28***

A solution of *syn*-(tetramethylene)bimane **26** (1.2 g, 5.0 mmol) in dioxane (50 mL) was treated with DDQ (2.3 g, 10.0 mmol). The solution was heated at 100°C for 24 h as the reaction was monitored with thin-layer chromatography (dichloromethane). After cooling a yellow precipitate was removed by filtration and the solvent was concentrated to give a dark brown residue which was redissolved in a minimal amount of dichloromethane and purified by chromatography (silica gel column, dichloromethane). The first fraction contained *syn*-(benzo) bimane **28** as a yellow solid (0.25 g, 29%), mp 308–310°C; H NMR ($CDCl_3$): δ 7.3–8.0 (m); UV (CH_3CN): λ (ε) 420 (6910); fluorescence (50% aqueous ethanol): λ (Φ) 428 (0.9) (reference quinine sulfate Φ 0.55) [27]; EI-MS: 236 (M^+). Anal. calcd for $C_{14}H_8N_2O_2$: C, 71.18; H, 3.41; N, 11.86. Found: C, 71.11; H, 3.41; N, 11.79. The following fraction contained *syn*-(benzo)(tetramethylene)bimane **27** (0.51 g, 58%) as a yellow solid, mp 226–227°C; H NMR ($CDCl_3$): δ 1.88 (m, 4 H), 2.32 (m, 2 H), 2.80 (m, 2 H), 7.10–7.90 (m, 4 H); UV (CH_3CN): λ (ε) 390 (8400); fluorescence (dioxane): λ (Φ) 435 (0.4); EI-MS: 240 (M^+). Anal. calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.87; H, 4.92; N, 11.56. *syn*-(Tetramethylene)bimane **26** (0.30 g) was recovered in the final fraction. When five equivalents of DDQ were employed all of the starting material was converted: *syn*-(benzo)bimane **28** (0.85 g, 72%) was obtained and only a trace amount of *syn*-(benzo) (tetramethylene)bimane **27** was detected by thin-layer chromatography.

4,6-Dibromo-1,2,3,4,6,7,8,9-octahydro-10H,12H-indazolo[1,2-a]indazol-10,12-dione **29**

A solution of bromine (1.6 g, 10.0 mmol) in dichloromethane (20 mL) was added dropwise in the dark to a solution of *syn*-(tetramethylene)bimane **26** (1.2 g, 5.0 mmol) in dichloromethane (30 mL). The reaction mixture was stirred for 15 h as a deep-red solution gradually changed to orange. The solution was washed (aqueous sodium bicarbonate), dried (magnesium sulfate), concentrated, and the residue recrystallized from acetonitrile to give the dibromoindazoloindazoldione **29** as a yellow crystalline solid, 1.85 g (92%); mp 142–143°C; H NMR ($CDCl_3$): δ 1.85–2.67 (m, 12 H), 5.57 (m, 2 H); EI-MS: 402 (M^+). Anal. calcd for $C_{14}H_{14}N_2O_2Br_2$: C, 41.82; H, 3.51; N, 6.97; Br, 39.74. Found: C, 41.57; H, 3.43, N, 6.87; Br, 39.66.

DDQ (1.1 g, 5.0 mmol) and the indazoloindazoldione **29** (0.4 g, 1.0 mmol) were dissolved in dioxane (50 mL). The solution was heated at reflux for 24 h as the reaction was monitored with thin-layer chromatography (dichloromethane) until the starting material **29** was consumed. *syn*-(Benzo)bimane **28**, the major product, was detected by thin layer chromatography.

1,2,4,5-Tetrahydro-3H-benz[g]indazol-3-one **38**

Hydrazine monohydrate (10.0 g, 0.2 mol) was added dropwise to a solution of ethyl 1,2,3,4-tetrahydro-1-oxo-2-naphthoate **37** (43.6 g, 0.2 mol) in methanol (100 mL). After an exothermic reaction subsided the solution was heated at reflux for 2 h, and cooled to give a colorless precipitate that was isolated and recrystallized from hot methanol to give the indazolone **38**, 23.2 g (62%), mp 214–215°C; H NMR (DMSO-d_6): δ 2.70 (q, 4 H, CH_2), 7.13–7.63 (m, 4 H, aromatic); EI-MS: 186 (M^+). Anal. calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.03. Found: C, 70.70; H, 5.46; N, 15.14.

1H-Benz[g]indazol-3-ol **40**

A sample of palladium (10% on charcoal) was added to a solution of the indazolone **38** in 1,2-dichlorobenzene (5 mL). The mixture was heated at reflux for 2 days as the reaction was monitored with thin-layer chromatography (dichloromethane). The catalyst was isolated, the solvent was removed, and an ivory solid residue was recrystallized from isopropanol to give the benzindazole **40**, 0.39 g (78%), mp 245–247°C (dec.); H NMR (DMSO-d_6): δ 3.70. Anal. calcd for $C_{11}H_8N_2O$: C, 71.73; H, 4.38; N, 15.21. Found: C, 71.58; H, 4.40; N, 14.83.

3a-Chloro-2,3a,4,5-tetrahydro-3H-benz[g]indazol-3-one **39**

Chlorine gas was slowly passed into a suspension of the indazolone **38** (20.0 g, 0.1 mol) in dichloromethane (250 mL) as the solid gradually dissolved. The yellow solution was stirred for 30 min and the solvent was removed to give a solid that recrystallized from a mixture of benzene and petroleum ether to give the chloroindazolone **39**, 17.6 g (74%), 200–205°C (dec); H NMR ($CDCl_3$-DMSO-d_6): δ 2.30 (m, 2 H, CH_2), 3.10 (m, 2 H, CH_2), 7.20–7.90 (m, 4 H, aromatic, 11.72 (s, 1 H, NH). Anal. calcd for $C_{11}H_9N_2OCl$: C, 59.88; H, 4.11; N, 12.70; Cl, 16.33. Found: C, 59.62; H, 4.08; N, 12.45; Cl, 16.07.

5,6,10,11-Tetrahydro-7H,9H-benz[6,7]indazolo[1,2-a]benz[g]indazol-7,9-dione **35**

Potassium carbonate sesquihydrate (22.0 g, 0.13 mol) was added in one portion to a solution of the chloroindazolone **39** (11.0 g, 0.05 mol) in dichloromethane (100 mL). The mixture was stirred at room temperature as the reaction was monitored with thin-layer chromatography (dichloromethane). After the reaction was completed (16 h) the mixture was chromatographed (silica gel column, dichloromethane) to give an orange solid that was purified from a mixture of isopropanol and acetonitrile as the bimane **35**, 4.5 g (53%), mp 265–267°C; H NMR (($CDCl_3$): δ 2.58 (t, 4 H, CH_2), 2.99 (t, 4 H, CH_2), 7.03–7.38 (m, 8 H, aromatic); UV (CH_3CN): λ (ε) 419 (3137); EI-MS: 340 (M^+). Anal. calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.27%. Found: C, 77.66; H, 4.83; N, 8.28%.

syn-(*α-Naphtho*)*bimane* **36**

A sample of palladium (10% on charcoal) (0.1 g) was added to a solution of the bimane **35** (3.4 g, 0.01 mol) in 1,2-dichlorobenzene (10 mL). The mixture was heated at reflux temperature for 2 days as the reaction was monitored with thin-layer chromatography (dichloromethane). Removal of the catalyst and solvent left a red residue that was purified (reprecipitated) from a mixture of hexafloropropan-2-ol and methanol, as *syn*-(α-naphtho)bimane **36** as a yellow powder, 2.4 g (71%); mp 313–315°C; H NMR ($CDCl_3$): δ 7.30–7.90 (m); UV (CH_3CN): λ (ε) 460 (10,201); fluorescence (CH_2Cl_2): λ (Φ) 492 (0.1); EI-MS: 336 (M^+). Anal. calcd for $C_{22}H_{12}N_2O_2$: C, 78.56; H, 3.60; N, 8.33. Found: C, 78.35; H, 3.66; N, 8.10. In the absence of a crystalline form an x-ray crystallographic analysis for the bimane **36** was not determined.

Acknowledgments

Financial assistance was received from ONR, ARO, Naval Weapons Center (China Lake, CA), and the Louisiana Board of Regents (LEQSF-RD-B-06). T.G.P. wishes to thank Naval Ocean Systems Center Independent Research program for support.

References

[1] P. P. Sorokin, J. R. Lankard, *IBM J. Res. Dev., 10,* 1966, 162.

[2] M. Maeda, *Laser Dyes,* Academic Press, Tokyo, 1984, pp 1–6.

[3] K. H. Drexhage, Structure and properties of laser dyes, in F. P. Shafer, (ed): *Topics in Applied Physics,* Springer, Berlin, 1973, pp 144–179.

[4] Exciton Laser Dye Catalog, Exciton, Inc., Dayton, OH, 1989.

[5] (a) T. G. Pavlopoulos, J. H. Boyer, I. R. Politzer, C. M. Lau, *J. Appl. Phys., 60,* 1986, 4028; (b) T. G. Pavlopoulos, C. J. McBee, J. H. Boyer, I. R. Politzer, C. M. Lau, *J. Appl. Phys., 62,* 1987, 36; (c) T. G. Pavlopoulos, J. H. Boyer, I. R. Politzer, C. M. Lau, *Optics Commun.,* 64, 1987, 367; (d) T. G. Pavlopoulos, J. H. Boyer, U.S. Patent 4,799,230 (1989).

[6] E. M. Kosower, B. Pazhenchevsky, *J. Am. Chem. Soc., 102,* 1980, 4983.

[7] E. M. Kosower, B. Pazhenchevsky, H. Dodiuk, M. Ben-Shoshan, H. Kanety, *J. Org. Chem., 46,* 1981, 1673.

[8] E. M. Kosower, B. Pazhenchevsky, H. Dodiuk, H. Kanety, D. Faust, *J. Org. Chem.,* 46, 1981, 1666.

[9] R. H. Wiley, P. Wiley: Pyrazolones, pyrazolidinones, and derivatives, in A. Weissburger (ed): *The Chemistry of Heterocyclic Compounds,* Wiley-Interscience, New York, 1964, p. 19.

[10] W. L. F. Armarego: Ultraviolet spectra of heterocycles, in A. R. Katritzky (ed): *Physical Methods in Heterocyclic Chemistry,* Academic Press, London, 1971, p. 81.

[11] H. Leisman, G. Marzolph, H.-D. Scharf, M. Behruzi, *Chem. Ber., 116,* 1983, 2591.

[12] S. K. Suri, K. Thangaraj, A. K. S. Bhujanga Rao, R. S. Prasad, C. Gundu Rao, S. P. Bhatnagar, *Chem. Ind.,* 1988, 94.

[13] F. Schmidt and K. Schoenafinger, Ger. Offen. 2855193; *Chem. Abstr., 94,* 1981, 48839.

[14] J. H. Boyer, *Nitroazoles,* VCH Publishers, Deerfield Beach, FL, 1986, pp 196–199.

[15] B. Hepner, A. Simonberg, *Bull. Soc. Chim., 6,* 1939, 1069.

[16] Work in collaboration with Dr. Geoffrey Lindsay, Naval Weapons Center, China Lake, CA.

[17] F. Ullmann, *Ann., 355,* 1907, 312.

[18] G. Heller, *Ber., 49,* 1916, 523.

[19] H. U. Immer, J. F. Bagli, Can. 847916; *Chem. Abstr., 73,* 1970, 120414s.

[20] T. G. Pavlopoulos, J. H. Boyer, C. M. Lau, I. R. Politzer, *Spec. Chim. Acta* A, *45A,* 1989, 1057.

[21] A rough estimate RE 66 was previously reported [5a].

[22] E. M. Kosower, D. Faust, M. Ben-Shoshan, I. Goldberg, *J. Org. Chem., 47,* 1982, 214.

[23] D. Basting, F. P. Shafer, B. Steyer, *Appl. Phys., 3,* 1974, 81; [2], p 291.

[24] M. Sapir, E. Vander Donckt, *Chem. Phys. Lett., 36,* 1975, 108.

[25] J. Kohlmannsperger, *Z. Naturforsch., 24a,* 1969, 1547; [2], p 147.

[26] T. G. Pavlopoulos, *Spectrochim. Acta, 42A,* 1986, 47.

[27] We are indebted to Dr. Robert Kubin, Naval Weapons Center, China Lake, CA for this determination from a mixture (1 : 1) of water and ethanol, with reference to quinine sulfate.

[28] T. G. Pavlopoulos, D. J. Golich, *J. Appl. Phys., 64,* 1988, 52.

[29] D. J. McClure, *J. Chem. Phys., 19,* 1951, 670.

[30] BIOGRAF Version 1.50, BioDesign Inc., Pasadena, CA, 1988.

[31] (a) N. L. Allinger, *J. Am. Chem. Soc., 99,* 1977, 8127; (b) T. Liljefors, J. C. Tai, S. Li, and N. L. Allinger, *J. Comp. Chem., 8,* 1987, 1051.

[32] H. Kanety, H. Dodiuk, E. M. Kosower, *J. Org. Chem., 47,* 1982, 207.

[33] O. Ochi, T. Miyasaka, and K. Arakawa, *Bull. Chem. Soc. Jpn., 50,* 1977, 2991.

[34] T. Kato, H. Yamanaka, F. Hamaguchi, *Yakugaku Zasshi, 83,* 1963, 741; *Chem. Abstr.,* 59, 1963, 13694g.

Heteroatom Chemistry
Volume 1, Number 5, 1990

Pyrromethene–BF_2 Complexes as Laser Dyes:1.

Mayur Shah, Kannappan Thangaraj, Mou-Ling Soong, Lionel T. Wolford, and Joseph H. Boyer*

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148, U.S.A.

Ieva R. Politzer

Department of Chemistry, Xavier University, New Orleans, Louisiana 70125, U.S.A.

Theodore G. Pavlopoulos

U.S. Naval Ocean Systems Center, San Diego, California 92152, U.S.A.

Received 17 April 1990.

ABSTRACT

Condensations between 3-X-2,4-dimethylpyrroles (X = H, CH_3, C_2H_5, and $CO_2C_2H_5$) and acyl chlorides gave derivatives of 3,5,3',5'-tetramethylpyrromethene (isolated as their hydrochloride salts): 6-methyl, 6-ethyl, 4,4',6-trimethyl, 4,4'-diethyl-6-methyl, and 4,4'-dicarboethoxy-6-ethyl derivatives for conversion on treatment with boron trifluoride to 1,3,5,7-tetramethylpyrromethene–BF_2 complex (TMP–BF_2) and its 8-methyl (PMP–BF_2), 8-ethyl, 2,6,8-trimethyl (HMP–BF_2),2,6-diethyl-8-methyl (PMDEP–BF_2), and 2,6-dicarboethoxy-8-ethyl derivatives. Chlorosulfonation converted 1,3,5,7,8-pentamethylpyrromethene–BF_2 complex to its 2,6-disulfonic acid isolated as the lithium, sodium (PMPDS–BF_2), potassium, rubidium, cesium, ammonium, and tetramethylammonium disulfonate salts and the methyl disulfonate ester. Sodium 1,3,5,7-tetramethyl-8-ethylpyrromethene-2,6-disulfonate–BF_2 complex was obtained from the 8-ethyl derivative of TMP–BF_2. Nitration and bromination converted PMP–BF_2 to its 2,6-dinitro- (PMDNP–BF_2) and 2,6-dibromo- derivatives. The time required for loss of fluorescence by irradiation from a sunlamp showed the following order for P–BF_2 compounds (10^{-3} to 10^{-4} M) in ethanol: PMPDS–BF_2, 7 weeks; PMP–BF_2, 5 days; PMDNP–BF_2, 72 h; HMP–BF_2, 70 h; and PMDEP–BF_2, 65 h. Under similar irradiation PMPDS–BF_2 in water lost fluorescence after 55 h. The dibromo derivative was inactive, but each of the other pyrromethene–BF_2 complexes under flashlamp excitation showed broadband laser activity in the region λ 530–580 nm. In methanol PMPDS–BF_2 was six times more resistant to degradation by flashlamp pulses than was observed for Rhodamine-6G (R-6G). An improvement (up to 66%) in the laser power efficiency of PMPDS–BF_2 (10^{-4} M in methanol) in the presence of caffeine (a filter for light <300 nm) was dependent on flashlamp pulse width (2.0 to 7.0 μsec).

INTRODUCTION

In 1984, less than two decades after its discovery, a review described the dye laser as one of the most useful and practical of tunable coherent sources; it became serviceable over the spectral region 300 to 1300 nm by the frequency agility of over 600 laser dyes, including cyanine, xanthene (e.g., rhodamine and fluoroscein), triarylmethane, acridine, azine, chlorophyll, polybenzenoid, coumarin, quinolone, oxazole, pyrazoline, and furan derivatives. Rhodamine dyes, for example, R-6G, gave laser activity over the spectral range 530–710 nm and were cited as the most important and most efficient group of all laser materials [1]. Laser dye activity was presumed to reflect a causal relationship with various ancillary properties, including photostability, solubility and other interactions with solvent, fluorescence quantum yield, molar extinction

*To whom correspondence should be addressed.

1042-7163/90/$3.50 + .25

of absorption, and minimal overlap of fluorescence with onset of absorption spectral regions (S–S) and triplet–triplet (T–T) [1,2]. Bathochromic and hyperchromic shifts were introduced by the substitution of auxochromic and antiauxochromic groups, but this benefit was often offset by the ability of certain groups, for example, nitro, cyano, and heavy atoms, to quench laser activity [1–3]. Since the known dyes were each deficient in one or more properties the search for new stuctures to offer superior performance standards was undertaken.

A recognition that the family of *syn*-bimanes **A** offered examples fulfilling many of the auxiliary conditions led to our discovery of their laser activity at 500–530 nm. Four bimanes **A1–4** were as efficient (80–100%) as coumarin 30 (coumarin 515) (laser activity in the same range) and showed improvements in photostability and solvent effects, and diminished overlap between fluorescence and absorption spectral regions (S–S and T–T) [3]. More recently the properties of certain pyrromethene–BF_2 complexes **10** and **11** also afforded candidates for laser dyes. We discovered laser activity at 533 nm from 1,3,5,7-tetramethylpyrromethene–BF_2 complex (TMP–BF_2) **10a** in methanol in 1988 [4]. Superior activity was rapidly discovered in 1,3,5,7,8-pentamethylpyrromethene–BF_2 complex (PMP–BF_2) and its 2,6-dimethyl (HMP–BF_2), 2,6-diethyl (PMDEP–BF_2), and 2,6-disulfonic acid (isolated as the disodium salt PMPDS–BF_2) derivatives [5,6]. Modest laser activity in the 2,6-dinitro derivative (PMDNP–BF_2) was exceptional [6] insofar as similar activity was not known for other dyes containing a nitro substituent. We report here on the synthesis of pyrromethene–BF_2 complexes and further discovery and development of them as laser dyes.

BACKGROUND INFORMATION

A generally efficient condensation between an α-acylpyrrole and a pyrrole unsubstituted at an α-position was developed as a classical synthesis of the pyrromethene precursors to porphyrins [7]. More recently the condensation reaction accommodated investigations on the pyrromethene chromophore and fluorophore in tailored derivatives that included P–BF_2 compounds [4, 5, 8, 9]. When expressed in a simplified version $[R_2N(CR{=}CR)_n CR{=}NR_2]^+$ the cationic chromophore of a cyanine dye [1] included the pyrromethene cation (n = 4); however, the role of the latter has been limited to P–BF_2 compounds for laser activity [4–6], fluorescent probes for medical and biological research [10], and photodynamic therapy for cancer [11].

The unsubstituted pyrromethene **B1** was unstable above −30°C and gave a yellow solution (λ_{max} 400 nm) in *n*-pentane moistened with methanol at −60°C [12]. Extensive alkylation brought about a bathochromic shift from 400 nm (log ϵ 4.35) for 3,5-dimethylpyrromethene **B2** in pentane [12] to 447 nm (log ϵ 4.53) for 3,5,3′,5′-tetramethyl-4,4′-diethylpyrromethene **B3** in ethanol [13]. Further bathochromic and hyperchromic shifts to 488 nm (log ϵ 5.00) and 528 nm (log ϵ 4.71) revealed related cationic pyrromethene chromophores for the hydrobromide and BF_2–complex derivatives **C** and **D** of the pyrromethene **B3** [10, 14, 15]. The band near 440 nm was shown to be polarized parallel to the long axis of the chromophore, whereas shorter wavelength bands were shown to be perpendicular to the long axis [16].

The nearly identical fluorescence quantum yields Φ 2.6 × 10^{-4} and 4.3 × 10^{-4} in ethanol, were descriptive of comparable fluorophores for 3,5,3′,5′-tetramethyl-4,4′-diethylpyrromethene **B3** and its hydrobromide **C** [17]. To account for these low quantum yields fluorescence quenching in a pyrromethene was variously correlated with proton tunneling [9], proton exchange between nitrogen atoms in the **Z** syn conformation, and photoisomerization at the exocyclic double bond [18, 19]; however, a deactivation of a pyrromethene S_1 state via exciplex formation, a process well known for polyamines [20], was not incompatible with the available information.

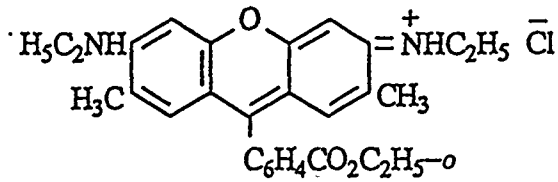
Chelation of boron difluoride by a pyrromethene bidentate anion was achieved by a treatment of a pyrromethene with boron trifluoride. Characterization of various pyrromethene–BF_2 (P–BF_2) derivatives included large extinction coefficients log $\epsilon \sim 5$ (comparable to the extinction coefficient shown for unchelated pyrromethene cations) and fluorescence quantum yields Φ 0.33 to 0.81 [14, 17]. A similar value Φ 0.31 was obtained for the corresponding $B(C_2H_5)_2$ complex **E** [17]. This thousandfold enhancement in fluorescence that was brought about by boron chelation with the pyrromethene bidentate ligand was reminiscent of a similar fluorescence enhancement that was recently attributed to the chelation of zinc dichloride by the diamino moieties in the nonfluorescent 9,10-bis(((2-(dimethylamino)ethyl)methylamino)methyl)anthracene **F**; fluorescence quenching in the tetramine **F** was attributed to exciplex formation [21].

Strong fluorescence in a bidentate BF_2 complex with nitrogen and/or oxygen atoms as ligand termini was afforded by P–BF_2 derivatives **10** and **11** (Scheme 1) and by the recently patented dicarbonyl chelates **G** (laser activity range 455–635 nm) [22]. Although fluorescence was noted for BF_2 complexes **H** [23] and **J** [24] from 1-amino-7-imino-1,3,5-cycloheptatrienes and 8-amino- and 8-hydroxyquinoline these complexes were not examined for laser activity. BF_2 complexes with less unsaturation, for example, the hexahydropyrromethene–BF_2 complex **K** with λ_{max} (C_2H_5OH) 320 nm (log ϵ 4.4) [25], were not examined for fluorescence (<400 nm) and laser activity. The hypsochromic shift ~120 nm relating P–BF_2 derivatives (λmax ~440 nm) and the

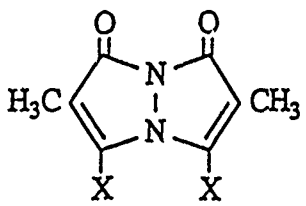
partially reduced structure **K** was typical of other cyanine dyes [1]. The structure assignment for PMP–BF_2 **10b** was supported by an X-ray crystallographic analysis [26].

Chelation of aluminum dichloride by a pyrromethene bidentate ligand gave an unstable orange solid; light absorption and emission data were not reported [25]. A different type of pyrromethene (P)–metal (M) chelate (P_2M) afforded by tetracoordinate zinc, nickel, and copper showed weak fluorescence above 500 nm ($\Phi \sim 10^{-3}$) [16, 18]. Pyrazoboles (dimeric 1-borylpyrazole chelates of dialkylboron (BR_2)) and the BF_2 complexes of 1,2,3,4-tetrahydro-1,10-phenanthroline were not fluorescent [27, 28].

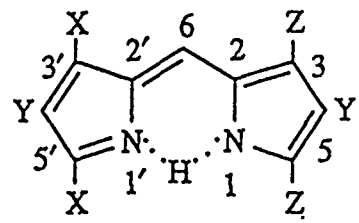
Laser activity was reported for a "boratriazinium" salt **L** and a "boradiazinium" salt **M**; however, preparations and structure characterizations for these molecules have not appeared in the literature [29].



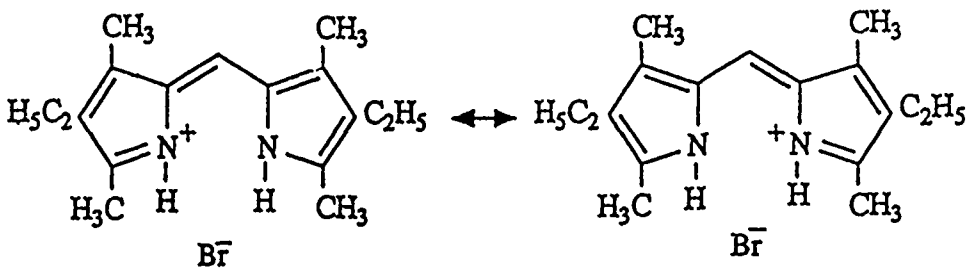
R - 6G·HCl



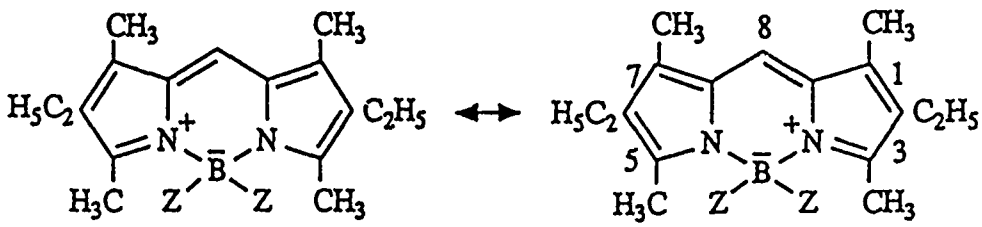
A1 X = $CH_2O_2CCH_3$
A2 X = $CH_2P(O)(OCH_3)_2$
A3 XX = $CH_2C(CO_2C_2H_5)_2CH_2$
A4 XX = $CH_2C(CO_2CH_3)_2CH_2$



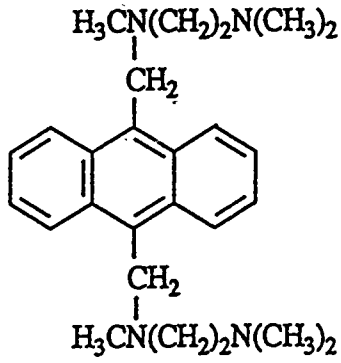
B1 X = Y = Z = H
B2 X = Y = H, Z = CH_3
B3 X = Z = CH_3, Y = C_2H_5



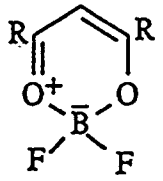
C



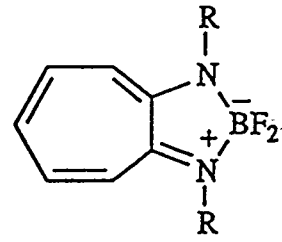
D Z = F
E Z = C_2H_5



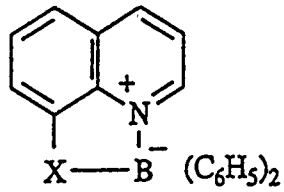
F



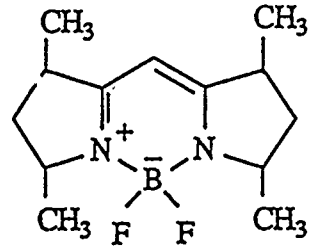
G R = $(CH{=}CH)_nAr$



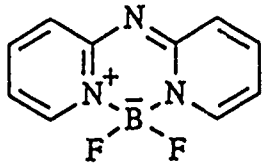
H



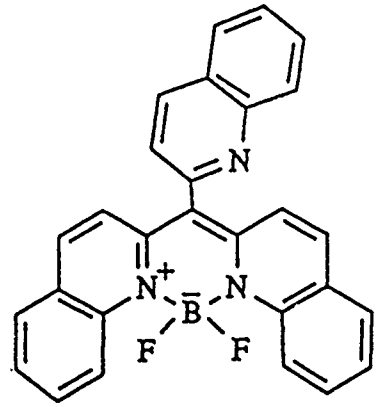
J X = NR, O



K



L

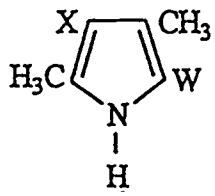


M

RESULTS AND DISCUSSION

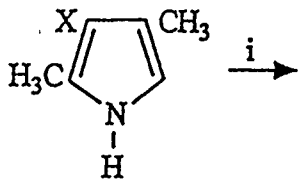
Synthesis

A general pathway shown in Scheme 1 was followed for the conversion of pyrroles **1–4** to P–BF_2 **10b–f**. Kryptopyrrole **3** was commercially available; the pyrroles **1**, **2**, and **4** were obtained by adapting reported procedures for the hydrolysis and decarboxylation of diethyl 3,5-dimethyipyrrole-2,4-dicarboxylate **5** [30, 31] and ethyl 3,4,5-trimethylpyrrole-2-carboxylate **6** [32, 33] and the thermolysis of *tert*-butyl 3,5-dimethyl-4-carboethoxypyrrole-2-carboxylate **7** [34]. In reactions with appropriate acyl chlorides pyrroles **1–4** afforded the unstable intermediate pyrromethene derivatives **9b–f**. These intermediates were isolated as hydrochloride salts and immediately converted, sometimes without purification, to their P–BF_2 derivatives **10b–f**. As C-substitution increased the pyrromethene hydrochlorides became more stable and more amenable to isolation and characterization. According to a previously reported procedure 2-formyl-3,5-dimethylpyrrole **8** and 2,4-dimethylpyrrole **1** gave unisolated 3,5,3′,5′-tetramethylpyrromethene **9a** [14].

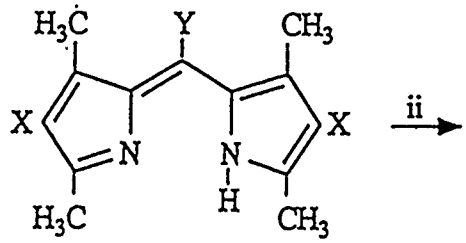


5 W = X = $CO_2C_2H_5$
6 W = $CO_2C_2H_5$, X = CH_3
7 W = $CO_2C(CH_3)_3$, X = $CO_2C_2H_5$
8 W = CHO, X = H

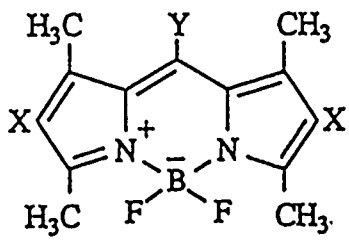
In a typical chelation the hydrochloride salt of 3,5,3′,5′-tetramethylpyrromethene **9a** gave TMP–BF_2 **10a** by treatment with boron trifluoride in the pres-



1–4



9a–f



10a–f

i = YCOCl; ii = $BF_3{\cdot}O(C_2H_5)_2$, R_3N

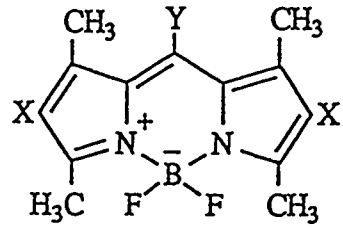
1 X = H; **2** X = CH_3; **3** X = C_2H_5; **4** X = $CO_2C_2H_5$

a X = Y = H; **b** X = H, Y = CH_3; **c** X = H, Y = C_2H_5;

d X = Y = CH_3; **e** X = C_2H_5, Y = CH_3;
f X = $CO_2C_2H_5$, Y = C_2H_5

11k, m $\xleftarrow{iv}$ **10b** $\xrightarrow{iii}$ **11a–j**

iii = $ClSO_3H$, base; iv = HNO_3 (k); Br_2 (m)



11 a–m, Y = CH_3; **11n**

a–e X = SO_3M, M = H (a), Li (b), Na (c), K (d), Rb (e), Cs (f);

g X = SO_3NH_4; **h** X = $SO_3N(CH_3)_4$; **j** X = SO_3CH_3; **k** X = NO_2; **m** X = Br; **n** X = SO_3Na, Y = C_2H_5

SCHEME 1

ence of triethylamine [14], or diisopropylethylamine (preferred) [16]. A similar conversion of the pyrrole derivative **4** afforded diethyl 1,3,5,7-tetramethyl-8-ethylpyrromethene-2,6-dicarboxylate-BF_2 complex **10f** [25]. To extend the method to the preparation of PMP–BF_2 **10b**, the precursor 3,5,3′,5′,6-pentamethylpyrromethene **9b** was obtained directly from the treatment of 2,4-dimethylpyrrole **1** with acetyl chloride. A similar preparation afforded the 8-ethyl- derivative **10c** from the precursor 3,5,3′,5′-tetramethyl-6-ethylpyrromethene **9c**, which was in turn obtained from 2,4-dimethylpyrrole **1** and propionyl chloride. Complete C-substitution in a pyrromethene and its BF_2–complex was rarely encountered. In addition to the complex **10f** other examples were found in chelations affording 1,2,3,5,6,7,8-heptamethyl- and 1,3,5,7,8-pentamethyl-2,6-diethyl-pyrromethene–BF_2 complexes (HMP–BF_2 and PMDEP–BF_2) **10d, 10e.**

Electrophilic sulfonation in the 2- and 6- positions was reported for the complex **10a** [15]. A similar substitution was initially useful in the preparation of the disodium (PMPDS–BF_2) and dimethyl 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate–BF_2 complexes **11c** and **11j**. Straightforward modifications led to the formation of other dimetal (Li, K, Rb, and Cs) salts **11b** and **11d–f** and the diammonium and the bistetramethylammonium 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate–BF_2 complexes **11g** and **11h**. Other examples of complete C-substitution were discovered in electrophilic nitration and bromination to give the 2,6-dinitro (PMDNP–BF_2) and 2,6-dibromo derivatives **11k** and **11m**. These substitution reactions were considered to be supportive of quasiaromaticity for the pyrromethene–BF_2 complexes (cf., **D**). This property is characteristic of various metal chelates [35, 36] and is further supported by proton nmr signals ∂ 6.00 to 7.62 for unsubstituted ring positions in P–BF_2 derivatives [13].

Laser Activity

Laser activity for P–BF_2 complexes (Table 1) gave RE from 0 to 100. Presumably a heavy atom effect brought about inactivity (RE 0) for 2,6-dibromo-1,3,5,7,8-pentamethylpyrromethane–BF_2 complex **11m**. Each of the P–BF_2 complexes **10a–f** and **11a–n** showed high molecular extinction coefficients (log ϵ_s 4 to 5) and high fluorescence quantum yields Φ 0.3 to 1.0) (Table 1). Minimal T–T absorption in or near the fluorescence spectral region was determined for TMP–BF_2 **10a** [4], PMP–BF_2 **10b** [5] and PMPDS–BF_2 **11c** (Figure 1). A value ϵ_T (567) = 1.5 × 10^3 L/mole cm for PMDEP–BF_2 **10e** was exceptionally low in comparison with ϵ_T (570) = 7.9 × 10^3 L/mol cm and ϵ_T (580) = 6.6 × 10^3 L/mole cm for rhodamine dyes 560 and 575 [6]. To avoid self-quenching through aggregation a dye concentration of about 10^{-4} M was generally sought. A hypsochromic shift in fluorescence from 534 to 509 nm for PMPDS–BF_2 **11c** in water was brought about by dilution from 10^{-3} to 10^{-8} M and attributed to diminished aggregation as dilution increased [37]. Although methanol (preferred), ethanol, or water were solvents of choice for laser activity from many P–BF_2, other satisfactory solvents in certain instances included acetonitrile, chloroform, dimethylsulfoxide, *N,N*-dimethylformamide, dichloromethane, dioxane, ethyl acetate, ethylene glycol, and hexafluoroisopropanol. Since the use of water minimized problems of storage and disposal or recovery of large amounts of organic solvents, water soluble dyes were sought. Aqueous solutions also offered thermooptic properties of water that often improved laser activity [2].

Just as a reaction between a P–BF_2 complex and methanolic potassium hydroxide was attributed to the initial nucleophilic attack at the 8-position that led to destruction of the chromophore [25], a similar reaction was assumed to account in part for the loss of fluorescence from PMP–BF_2 **10b** in ethanol solution after exposure to sunlamp irradiation for 5 days. In contrast, the loss of fluorescence from the complex **10b** in dichloromethane required a similar exposure to irradiation for 21 days. A greater photolability was demonstrated in the loss of fluorescence from other P–BF_2 derivatives (10^{-4} M in ethanol): PMDNP–BF_2 **10k** after 72 h, HMP–BF_2 **10d** after 70 h, and PMDEP–BF_2 **10e** after 65 h; and from PMPDS–BF_2 **11c** (10^{-4} M in water) after 55 h. In methanol PMPDS–BF_2 **11c** was markedly more stable; the loss of fluorescence in a similar experiment required 7 weeks. When photostability was determined by the number of flashlamp pulses required to lower laser power efficiency by 50% the complex **11c** in methanol or ethanol was discovered to be much more photostable than other known laser dyes (including other P–BF_2 derivatives) for the spectral region 530–560 nm [38, 39]. In one laboratory, when methanol solutions were examined the complex **11c** was six times more photostable than the dye R-6G (9000 pulses vs. 1500 pulses) [40].

A comparison of laser energy output as a function of flashlamp pump energy showed PMPDS–BF_2 **11c** in ethanol offered three times the power efficiency from coumarin 545 and was comparable in efficiency to R-6G [5]. Because of its exceptional photostability in methanol, PMPDS–BF_2 **11c** was selected for further examination. From flashlamp excitation (pulsewidth 2 μsec, risetime 0.7 μsec) with pump energy at 300 J in conjunction with an LFDL-8 laser, a 30% improvement in power efficiency for PMPDS–BF_2 **11c** over R-6G (each 10^{-4} M in methanol) was realized [41, 42]. In the presence of caffeine (a filter for light <300 nm) PMPDS–BF_2 (10^{-4} M in methanol) gave an improvement (28% to 66%) in laser efficiency that was dependent on flashlamp pulse width (2.0 to 7.0 μsec) [38, 39]. In contrast with an enhancement in laser activity from 10^{-3} M aqueous solutions of R-6G and other xanthene dyes brought about by the presence of β-cyclodextrin (10^{-2} M), the fluorescence of PNPDS–BF_2 (10^{-3} to 10^{-8} M) in water was unaffected by similar treatment [37]. An interest in the effect on laser activity by the formation of a salt between R-6G (the free base) and 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonic acid **11a** was thwarted by the failure to obtain a tractable product from their interaction. There was no improvement in laser ac-

TABLE 1 Pyrromethene–BF_2 Complexes[a]

No.	λ_{max} nm	log ϵ	λ_{Fl} nm	Φ	λ_{las} nm	RE[b] %
10a	505	4.92	516	0.80	533	30
10b	493	4.90	519	0.99	542	100
10c	495	4.99	517	1.0	546	90
10d	518	4.67	543	0.70[c]	570	75
10e	517	4.81	546	0.83[c]	570	100
10f	493[d]	4.97[d]	531	0.38[c]	556	50
11b	497	4.96	533	0.62[c]	554	65
11c	492	4.86	533	0.73[e]	560	90
11d	498	4.96	534	0.78[e]	556	100
11e	497	4.91	533	0.88[e]	553	95
11f	497	4.91	531	0.81[e]	553	95
11g	496	4.92	533	0.90[e]	557	95
11h	497	4.97	535	0.89[e]	556	95
11j	483[f]	4.82	520[f]	0.82[g]	554[f]	35
11k	493	4.62	533	[h]	[h]	[h]
11m	516[f]	4.81	546[f]	0.45[g]		
11n	498	4.90	530	0.44[c]	555	50

[a]Methanol was used as solvent except where noted otherwise.
[b]Relative Efficiency in laser power output. RE 100 assigned to PMP–BF_2 **10b**. RE 30 observed for Coumarin 545 [5].
[c]In ethanol.
[d]λ_{max} 495 nm (log ϵ 5.26) [23].
[e]In water.
[f]In a mixture (9:1) of methanol and dichloromethane.
[g]In dichloromethane.
[h]Due to photoinstability the data was not reproducible.

TABLE 2 Pyrromethene–BF_2 Complexes

No.	Yield %	mp °C	Formula	Calculated, % Found, %
10b	66	254–257 dec	$C_{14}H_{17}N_2F_2B$	C, 64.15; H, 6.53; N, 10.74 C, 64.34; H, 6.71; N, 10.84
10c	45	214–216	$C_{15}H_{19}N_2F_2B$	C, 65.24; H, 6.92; N, 10.15 C, 64.97; H, 6.88; N, 10.05
10d	34	286–287 dec	$C_{16}H_{21}N_2F_2B$	C, 66.20; H, 7.24; N, 9.65 C, 66.23; H, 7.35; N, 9.57
10e	34	207–208	$C_{18}H_{25}N_2F_2B$	C, 67.92; H, 7.86; N, 8.80 C, 67.88; H, 8.06; N, 8.79
11b	84	>280	$C_{14}H_{25}N_2O_6F_2BS_2Li \cdot 2H_2O$	C, 35.74; H, 3.19; N, 5.95 C, 36.16; H, 3.50; N, 5.97
11c	75	> 300	$C_{14}H_{15}N_2O_6F_2BS_2Na_2$	C, 36.07; H, 3.24; N, 6.01 C, 36.42; H, 3.35; N, 6.14
11d	82	>280	$C_{14}H_{15}N_2O_6F_2BS_2K_2$	C, 33.79; H, 3.01; N, 5.62 C, 33.91; H, 3.02; N, 5.62
11e	62	>280	$C_{14}H_{15}N_2O_6F_2BS_2Rb_2$	C, 28.42; H, 2.53; N, 4.73 C, 28.36; H, 2.45; N, 4.69
11f	57	>280	$C_{14}H_{15}N_2O_6F_2BS_2Cs_2$	C, 24.49; H, 2.18; N, 4.08 C, 24.58; H, 2.18; N, 4.13
11g	60	>300	$C_{14}H_{23}N_4O_6F_2BS_2$	C, 36.85; H, 5.08; N, 12.28 C, 36.91; H, 5.02; N, 12.20
11h	78	281–282 dec	$C_{22}H_{39}N_4O_6F_2BS_2 \cdot H_2O$	C, 45.05; H, 7.05; N, 9.55 C, 45.29; H, 6.73; N, 9.50
11j	40	218–222 dec	$C_{16}H_{21}N_2O_6F_2BS_2$	C, 42.67; H, 4.70; N, 6.22 C, 42.54; H, 4.76; N, 5.96
11k	71	279–281 dec	$C_{14}H_{15}N_4O_4F_2B$	C, 47.70; H, 4.26; N, 15.90 C, 48.18; H, 4.46; N, 15.94
11m	50	300–302 dec	$C_{14}H_{15}N_2Br_2F_2B$	C, 40.00; H, 3.57; N, 6.66 C, 40.13; H, 3.67; N, 6.59
11n	69	>260	$C_{15}H_{17}N_2O_6F_2BS_2Na_2$	C, 37.52; H, 3.57; N, 5.84 C, 38.20; H, 3.79; N, 5.75

tivity from an equimolar mixture of the two dyes R-6G (as the hydrochloride salt) and PMPDS–BF_2 **11c**, in methanol.

EXPERIMENTAL

Spectral data was obtained from the following instruments: Pye-Unicam SP 200 and Sargent-Welch 3-200 IR, Varian EM 360A, and IBM AF200 NMR [43], Hewlett-Packard 5985 (70 eV) (GC-MS), Cary 17 (UV), and Perkin-Elmer LS-5B Luminescence Spectrometers. A dye laser was constructed at the Naval Ocean Systems Center [44]. It operated in the non-flowing (static) mode and had no tuning capability. The dye cell (2.5 mm diameter, 50 mm long) had an eliptical cavity configuration of small eccentricity. The flashlamp EG & G model FX 139C-2, produced a pulse that had a rise time of 200 ns, half-width length of 600 ns, and input energy of 2 J at 6.32 kV, 5 J at 10.00 kV, 7.2 J at 12.00 kV, and 10 J at 14.14 kV [44, 45]. Laser energy outputs were measured with an accuracy of ±5% by a Scientech 365 power and energy meter [46]. Light absorption, luminescence, and laser activity properties are described in Table 1.

For each product the IR and EI-MS data agreed with the literature data and/or supported the assigned structure. Each recorded UV absorption was restricted to the highest wave length. ^1H NMR spectra were run in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR were recorded at 22.5 MHz with the deuterated solvent as an internal reference; the central peak of the solvent multiplet signal was assigned: ∂ 77.00 ($CDCl_3$), 39.50 $(CD_3)_2(SO)$. Poor solubility precluded NMR analyses in many instances. Fluorescence quantum yields of the dyes were determined for methanol solutions with excitation at 450 and 460 nm by reference to acridine orange, φ 0.46 [14], in ethanol. Melting points were determined on a Thomas Hoover melting point apparatus and were uncorrected. Elemental analyses were obtained from Midwest Micro Lab, Indianapolis, Indiana and Galbraith Laboratories, Inc., Knoxville, Tenn. Solvents were removed by rotary evaporation under reduced pressure unless indicated otherwise. Column chromatography was performed on silica gel (various grades). Triplet extinction coefficients over the laser action spectral region of the dye were measured at the temperature of liquid nitrogen by equipment previously described [47] using McClure's method [48].

Solvents, reagents, and starting materials that

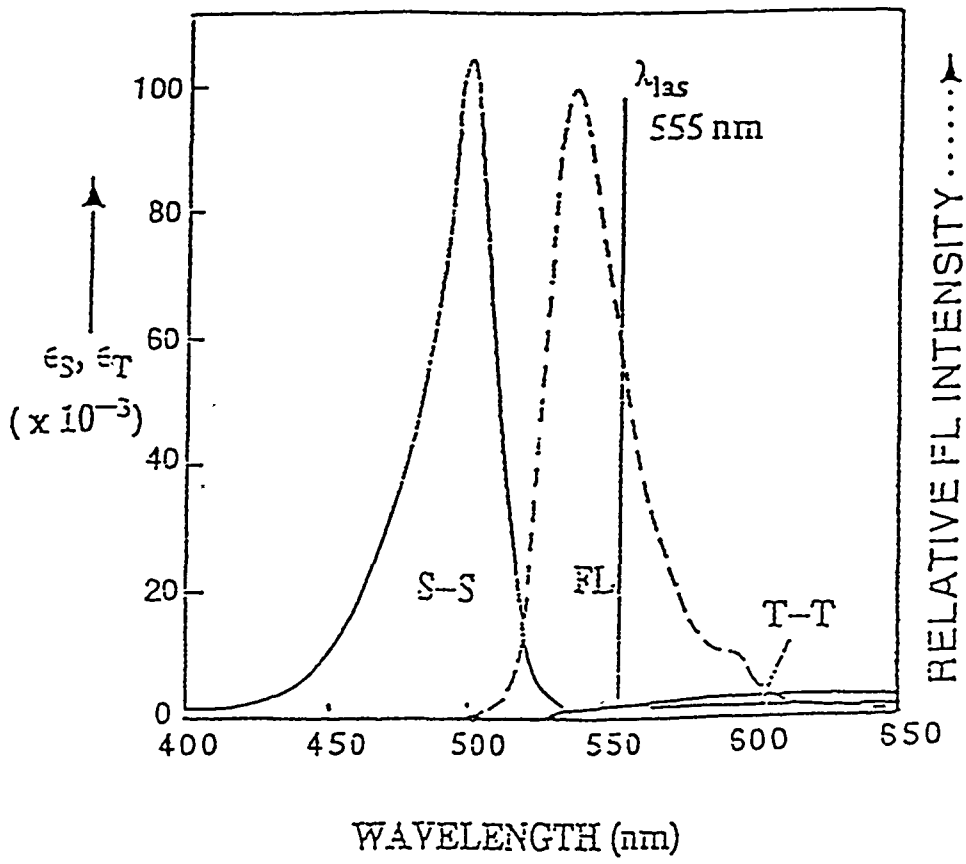


FIGURE 1 Absorption and luminescence for PMPDS–BF_2 complex **11c**. T–T absorption: 1×10^{-4} M in α-methyltetrahydrofuran at 77 °K. S–S absorption and fluorescence: 1×10^{-4} M in ethanol. Broadband laser action: 2×10^{-4} M in ethanol.

were obtained from the Aldrich Chemical Company, Milwaukee, WI included acetic anhydride, acetone, acetonitrile, acetyl chloride, alumina, ammonium carbonate, ammonium chloride, benzene, boron trifluoride etherate, bromine, carbon tetrachloride, celite, cesium carbonate, chloroform-d, chlorosulfonic acid, deuterium oxide, dichloromethane, *N,N*-disopropylethylamine, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide-d_6 (DMSO-d_6), *p*-dioxane, ethanol, ethyl acetate, hexane, hexafluoroisopropanol, hydrazine hydrate, lithium carbonate, isopropanol, isopropyl ether, kryptopyrrole (2,4-dimethyl-3-ethylpyrrole **3**), magnesium sulfate, methanol, nitric acid, 2-methyltetrahydrofuran, petroleum ether, phosphoric acid, potassium bromide, potassium carbonate, potassium fluoride, propionyl chloride, rubidium carbonate, silica gel (230–400 mesh, 60 Å), sodium bicarbonate, sodium hydroxide, sodium sulfate, tetrahydrofuran (THF), tetramethylammonium carbonate, toluene, triethylamine, and trifluoroethanol. Rhodamine 6G and thin layer chromatography sheets were obtained from Eastman Kodak Co., Rochester, NY. Chlorine was obtained from Matheson Gas Products, Secaccus, NJ. Nitrogen was obtained from Air Products and Chemicals, Inc., Allentown, PA.

The following compounds were prepared according to the directions cited: ethyl 2,4-dimethylpyrrole-3-carboxylate **4** [34]; diethyl 3,5-dimethylpyrrole-2,4-dicarboxylate **5** [30, 31]; ethyl 3,4,5-trimethylpyrrole-2-carboxylate **6** [32]; *tert*-butyl 3,5-dimethyl-4-carboethoxypyrrole-2-carboxylate **7** [34]; 2-formyl-3,5-dimethylpyrrole **8** [12]; 3,5,3′,5′-tetramethylpyrromethene **9a** (modified for isolation as its hydrochloride salt) [14]; 1,3,5,7-tetramethylpyrromethene–BF_2 complex **10a** (modified procedure) [14]; and 4,4′-dicarboethoxy-6-ethyl-3,5,3′,5′-tetramethylpyrromethene **9g** (modified for isolation as the hydrochloride derivative, mp 227–232°C (dec), EI-MS (relative abundance): 373 (100, $M^+ - Cl$)) [34].

2,4-Dimethylpyrrole **1**

In an adaptation of a procedure [30], diethyl 3,5-dimethylpyrrole-2,4-dicarboxylate **5** (160.0 g, 0.66 mol) as a melt at 140°C was treated with phosphoric acid (85%, 320 mL). The mixture was heated at 180°C for 30 min and poured into aqueous sodium

hydroxide (3.5 M, 3.5 L). Codistillation gave 3 L that was extracted with isopropyl ether (3 × 500 mL). The organic phase was dried (potassium carbonate) and concentrated to give a dark brown oil that distilled, 70–80°C (10 mm), to give 2,4-dimethylpyrrole **1** as a colorless oil, 40.00 g (64%); bp 162–165°C (lit. [30] 160–165°C), ^{1}H NMR ($CDCl_3$): ∂ 2.07 (s, 3H), 2.16 (s, 3H), 5.72 (s, 1H) 6.31 (s, 1H), 7.20–7.87 (br s, 1H). Similarly, ethyl 3,4,5-trimethyl-2-carboxylate **6** was converted to 2,3,4-trimethylpyrrole **2** as a colorless solid (67%), mp 37–38°C (lit. [32] mp 36–38°C).

3,5,3′,5′,6-Pentamethylpyrromethene Hydrochloride **9b**

Acetyl chloride (35 mL, 0.49 mol) was added dropwise with stirring over a period of 15 min to a solution of 2,4-dimethylpyrrole **1** (20.0 g, 0.21 mol) in dichloromethane (150 mL). The reaction mixture was heated at 40°C for 1 h, cooled to room temperature, diluted with petroleum ether (1.5 L), and triturated for 12 h to bring about the separation of 3,5,3′,5′,6-pentamethylpyrromethene hydrochloride **9b**. It was isolated by vacuum filtration as a red-brown powder, 24.0 g (91%), mp 180–185°C (dec); EI-MS (relative abundance): 214 (51.8) M^+ − HCl); ^{1}H NMR ($CDCl_3$); ∂ 2.02 (s, 6H); 2.20 (s, 6H); 2.49 (s, 3H); 6.20 (s, 2H) [43]. Instability precluded elemental analysis.

Similarly, the hydrochloride salts of derivatives of 3,5,3′,5′-tetramethylpyrromethene were obtained. The pyrrole **1** and propionyl chloride gave the 6-ethyl- derivative **9c**, 81%, mp 192–195°C (dec). Anal. Calcd. for $C_{15}H_{21}N_2Cl$: C, 68.04; H, 7.99; N, 10.58. Found: C, 67.47; H, 7.80; N, 10.17. The pyrrole **2** and acetyl chloride gave the 4,4′,6-trimethyl derivative **9d**, 80%, mp 210–212°C (dec); ^{1}H NMR ($CDCl_3$): ∂ 1.90 (s, 6H), 2.00 (s, 6H), 2.45 (s, 6H), 2.75 (s, 3H) [33]. Anal. Calcd. for $C_{16}H_{23}N_2Cl$: C, 68.94; H, 8.25; N, 10.05; Cl, 12.74. Found: C, 69.41; H, 7.72; N, 10.21; Cl, 12.97. The pyrrole **3** and acetyl chloride gave the 4,4′-diethyl-6-methyl derivative **9e**, 77%, mp 185–186°C (dec); ^{1}H NMR ($CDCl_3$): ∂ 1.01 (t, 6H), 2.07 (s, 6H), 2.35 (q, 4H), 2.46 (s, 6H), 2.76 (s, 3H) [43]. Anal. Calcd. for $C_{18}H_{27}N_2Cl$: C, 70.47; H, 8.80; N, 9.13; Cl, 11.58. Found: C, 70.67; H, 9.00; N, 9.15; Cl, 11.73.

1,3,5,7,8-Pentamethylpyrromethene–BF_2 Complex (PMP–BF_2) **10b**

Triethylamine (15 mL, 113 mmol) was added at room temperature to a suspension of 3,5,3′,5′,6-pentamethylpyrromethene hydrochloride **9b** (6.0 g, 24 mmol) in toluene (600 mL) and the mixture was stirred for 15 min. Boron trifluoride etherate (20 mL, 163 mmol) was added dropwise with stirring as a green fluorescence developed. The reaction mixture was heated (80°C) for 15 min, cooled to 40°C, washed with warm water (3 × 100 mL), dried (magnesium sulfate), and concentrated to give a dark brown solid. Flash chromatographic [49] separation of a solid mixture (silica gel, 250 g, 230–400 mesh, 60 Å, a mixture (80:20) of toluene and hexane), followed by concentration of the intense green-yellow fluorescent fractions, gave PMP–BF_2 **10b**. It recrystallized from ethyl acetate as an orange crystalline solid, 4.1 g (66%) (see Tables 1 and 2 for other properties). In reactions with boron trifluoride the hydrochlorides of pyrromethenes 9c–f gave the corresponding P–BF_2 derivatives **10c–f** (Table 1). ^{1}H NMR [43]: HMP–BF_2 **10d** ($CDCl_3$): ∂ 1.91 (s, 6H), 2.29 (s, 6H), 2.46 (s, 6H), and 2.57 (s, 3H); PMDEP–BF_2 **10e** ($CDCl_3$): ∂ 1.01 (t, 6H), 2.30 (s, 6H), 2.37 (q, 4H), 2.47 (s, 6H), and 2.57 (s, 3H).

Disodium 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate–BF_2 Complex (PMPDS–BF_2) **11c**

A solution of chlorosulfonic acid (3.26 g, 28 mmol) in dichloromethane (20 mL) was added dropwise to a suspension of PMP–BF_2 **10b** (3.65 g, 14 mmol) in dichloromethane (50 mL) at −50°C. A yellow solid separated as the reaction mixture warmed slowly to room temperature. The disulfonic acid **11a** was isolated by vacuum filtration and treated with water (600 mL). The aqueous solution was neutralized with sodium bicarbonate (2.52 g, 30 mmol). The solution was concentrated to 75 mL and treated with ethanol (400 mL) to bring about the separation of the salt **11c**. It was isolated by vacuum filtration, recrystallized from aqueous ethanol (80%), and dried in air to give a yellow-orange powder, 5.0 g (75%) (Table 1). The dilithium, dipotassium, dirubidium, dicesium, diammonium, and the bistetramethylammonium salts **11b, 11d–h** (Tables 1 and 2) were prepared in straightforward reactions. A similar conversion of 1,3,5,7-tetramethyl-8-ethylpyrromethene–BF_2 complex **10c** gave disodium 1,3,5,7-tetramethyl-8-ethylpyrromethene-2,6-disulfonate–BF_2 complex **11n** (Tables 1 and 2).

Dimethyl 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate–BF_2 Complex **11j**

A solution of chlorosulfonic acid (3.6 g, 30 mmol) in dichloromethane (20 mL) was added dropwise to a cooled suspension of 1,3,5,7,8-pentamethylpyrromethene–BF_2 complex **10b** (2.0 g, 7.6 mmol) in dichloromethane (30 mL) at −50°C. A brown oil separated as the clear yellow solution warmed to room temperature. It was treated with methanol (10 mL), stirred for 0.5 h at room temperature, concentrated to a brown viscous oil, treated with methanol (40 mL), and stirred to bring about the separation of a yellow-brown solid that was isolated by vacuum filtration, treated with methanol (100 mL), and heated (60°C) for 0.5 h to complete an esteri-

fication. The solid ester **11j**, 1.4 g (40%), was isolated and purified from methanol to give an orange-yellow powder (Tables 1 and 2).

1,3,5,7,8-Pentamethyl-2,6-dinitropyrromethene–BF_2 complex (PMDNP-BF_2) **11k**

After PMP–BF_2 **10b** (3.0 g, 11.5 mmol) was added to nitric acid (50 mL, 70%) at 0°C, the orange-red mixture was stirred at 0°C for 1.5 h and poured into ice water (200 mL) to precipitate the 2,6-dinitro derivative **11k** as an orange solid, isolated by filtration and washed with water. It recrystallized from ethyl acetate as an orange powder (2.9 g) (Tables 1 and 2).

1,3,5,7,8-Pentamethyl-2,6-dibromopyrromethene–BF_2 Complex **11m**

Bromine (16.0 g, 100 mmol) in dichloromethane (50 mL) was added dropwise to PMP–BF_2 **10b** (2.0 g, 7.6 mmol) in dichloromethane (150 mL) over a period of 10 min at 25°C with stirring. An orange precipitate was separated, triturated with dichloromethane (150 mL), and dried to give the dibromo derivative **11m** as an orange crystalline solid, 1.6 g (Tables 1 and 2); ^{1}H NMR [43] ($CDCl_3$): ∂ 2.41 (s, 6H), 2.55 (s, 6H), and 2.60 (s, 3H).

Pyrromethene–BF_2 Complexes Photostability

A solution of 1,3,5,7,8-pentamethylpyrromethene–BF_2 complex (PMP–BF_2) **10b** (0.10 g, 0.3 mmol) in ethanol (250 mL) was irradiated by a sunlamp (GE 275W) at a distance of 30 cm. Fluorescence at 500 nm became undetectable after 5 days. In similar experiments other P–BF_2 derivatives (10^{-4} M in ethanol) also lost fluorescence: PMDNP–BF_2 **11k** after 72 h, HMP–BF_2 **10d** after 70 h, and PMDEP–BF_2 **10e** after 65 h. Disodium 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate–BF_2 complex (PMPDS–BF_2) **11c** (2.0 mg) in water (50 mL) lost its fluorescence at 492 nm after 55 h of similar irradiation; when water was replaced with methanol the duration of fluorescence was 7 weeks. In brown bottles all P–BF_2 compounds were indefinitely stable to storage at 25°C.

ACKNOWLEDGMENTS

Financial assistance was received from ONR, ARO, Naval Weapons Center (China Lake, CA), and the Louisiana Board of Regents (LEQSF-RD-B-06). T.G.P. wishes to thank NOSC Independent Research program for support.

REFERENCES

[1] M. Maeda: *Laser Dyes*, Academic Press, Tokyo, Japan, 1984.
[2] C. M. Lau, I. R. Politzer, K. Thangaraj, G. Kumar, V. T. Ramakrishnan, E. D. Stevens, J. H. Boyer, and T. G. Pavlopoulos, *Heteroatom Chem., 1*, 1990, 195.
[3] H. Zollinger: *Color Chemistry*, VCH, Weinheim, 1987.
[4] T. G. Pavlopoulos, M. Shah, and J. H. Boyer, *Applied tics, 27*, 1988, 4998.
[5] T. G. Pavlopoulos, M. Shah, and J. H. Boyer, *Optics Commun., 70*, 1989, 425.
[6] T. G. Pavlopoulos, J. H. Boyer, M. Shah, K. Thangaraj, and M.-L. Soong, *Applied Optics*, submitted.
[7] A. H. Corwin: The Chemistry of Pyrrole and its Derivatives, in R. C. Elderfield (ed), *Heterocyclic Compounds*, Vol. 1, John Wiley and Sons, New York, pp. 277–342 (1950).
[8] S. E. Braslavsky, A. R. Holzwarth, and K. Schaffner, *Angew. Chem. Int. Ed. Engl., 22*, 1983, 656.
[9] J. A. Pardoen, J. Lugtenburg, and G. W. Canters, *J. Phys. Chem., 89*, 1985, 4272.
[10] E. Vos de Wael, J. A. Pardoen, J. A. Van Koeveringe, and J. Lugtenburg, *Recl. Trav. Chim. Pays-Bas, 96*, 1977, 306.
[11] L. R. Morgan, A. Chaudhuri, L. E. Gillen, J. H. Boyer, and L. T. Wolford: *Pentamethylpyrromethene boron difluoride complex in human ovarian cancer photodynamic therapy*, Optical Engineering/Laser '90 Conference, Los Angeles, CA, January 1990.
[12] J. A. Van Koeveringe and J. Lugtenburg, *Recl. Trav. Chim. Pays-Bas, 96*, 1977, 55.
[13] R. W. Guy and R. A. Jones, *Aust. J. Chem. 18*, 1965, 363.
[14] A. W. Johnson, I. T. Kay, E. Markham, R. Price, and K. B. Shaw, *J. Chem. Soc.*, 1959, 3416.
[15] H. J. Wories, J. H. Koek, G. Ladder, and J. Lugtenburg, *Recl. Trav. Chim. Pays-Bas, 104*, 1985, 288.
[16] H. Falk, O. Hofer, and H. Lehner, *Monatsh. Chem., 105*, 1974, 169.
[17] A. Holzwarth, H. Lehner, S. E. Braslavsky, and K. Schaffner, *Liebigs Ann. Chem.*, 1978, 2002.
[18] H. Falk and F. Neufingerl, *Monatsh. Chem., 110*, 1979, 987.
[19] H. Falk, K. Grubmayr, and F. Neufingerl, *Monatsh. Chem., 108*, 1977, 1185.
[20] M. Gordon and W. R. Ware (eds): *The Exciplex*, Academic Press, New York, 1975.
[21] M. E. Huston, K. W. Haider, and A. W. Czarnik, *J. Amer. Chem. Soc., 110*, 1988, 4460.
[22] H. Hartmann, R. Hultzsch, H. D. Ilge, B. Friedrich, J. Hebenstreit, D. Fassler, and U. Meinel, Ger. (East) DD 255,884; *Chem. Abstr., 104*, 1986, 139107z; P. Czerney, C. Igney, G. Haucke, and H. Hartmann, *Z. Chem.*, 1988, 23.
[23] H. E. Holmquist and R. E. Benson, *J. Amer. Chem. Soc., 84*, 1962, 4720.
[24] E. Hohaus and F. Umland, *Chem. Ber., 102*, 1969, 4025.
[25] A. Treibs and F.-H. Kreuzer, *Liebigs Ann. Chem., 718*, 1968, 208; A. Treibs and F.-H. Kreuzer, *Liebigs Ann. Chem., 721*, 1969, 116.
[26] C. L. Picou, E. D. Stevens, M. Shah, and J. H. Boyer, *Acta Cryst. Soc. C.*, in press.
[27] S. Trofimenko, *J. Amer. Chem. Soc., 89*, 1967, 3165, 3170; S. Trofimenko, *J. Amer. Chem. Soc., 92*, 1970, 5118.
[28] G. Klebe, K. Hensen, and H. Fuess, *Chem. Ber., 116*, 1983, 3125.
[29] D. Basting, F. P. Schafer, and B. Steyer, *Appl. Phys., 3*, 1974, 81.

[30] A. Treibs and L. Schulze, *Liebigs Ann. Chem., 739,* 1970, 225.
[31] H. Fischer, *Organic Syntheses, Coll. Vol II, 1943,* 202, 217.
[32] J. E. Bullock, A. W. Johnson, E. Markham, and K. B. Shaw, *J. Chem. Soc.,* 1958, 1430.
[33] P. S. Clezy and A. W. Nichol, *Aust. J. Chem., 11,* 1965, 1835.
[34] A. Treibs and K. Hintermeier, *Chem. Ber., 87,* 1954, 1167; A Treibs and K. Hintermeier, *J. Liebigs Ann. Chem., 592,* 1975, 11.
[35] J. P. Collman, *Angew. Chem. Intern. Ed. Engl., 4,* 1965, 132.
[36] J. P. Collman: "The Chemistry of Quasiaromatic Metal Chelates," *Advances in Chemistry Series,* No. 37, American Chemical Society, Washington, D. C., 1963, p 78.
[37] I. R. Politzer, K. T. Crago, S. Garner, J. Joseph, J. H. Boyer, and M. Shah, International Conference on Lasers '89, New Orleans, LA, December 1989, Technical Digest HN. 10.
[38] J. H. Boyer, M. Shah, T. G. Pavlopoulos, and S. E. Neister, Sixth European Symposium on Organic Compounds, Belgrade, Yugoslavia, September 1989, Book of Abstracts, p. 2.
[39] Personal communication from Dr. S. E. Neister, Phase-R Corporation
[40] Personal communication from Dr. J. J. Ehrlich and Wayne Davenport, U. S. Army Missile Command, Redstone Arsenal.
[41] J. H. Boyer, M. Shah, K. Thangaraj, L. T. Wolford, T. G. Pavlopoulos, and J. Hsia, International Conference on Lasers '89, New Orleans, LA, December 1989, Technical Digest HN. 11.
[42] Personal communication from Dr. James Hsia, Candela Corporation.
[43] We are indebted to Dr. Harry Ensley, Tulane University, for the use of the IBM instrument.
[44] T. G. Pavlopoulos, *Spectrochim. Acta, 42A,* 1986, 47.
[45] T. G. Pavlopoulos, J. H. Boyer, I. R. Politzer, and C. M. Lau, *J. Appl. Phys., 60,* 1986, 4028.
[46] T. G. Pavlopoulos, J. H. Boyer, I. R. Politzer, and C. M. Lau, *Optics Comm., 64,* 1987, 367.
[47] T. G. Pavlopoulos and D. J. Golich, *J. Appl. Phys., 64,* 1988, 52.
[48] D. J. McClure, *J. Chem. Phys, 19,* 1951, 670.
[49] W. Clark Still, M. Kahn, and A. Mitra, *J. Org. Chem., 43,* 1978, 2923.